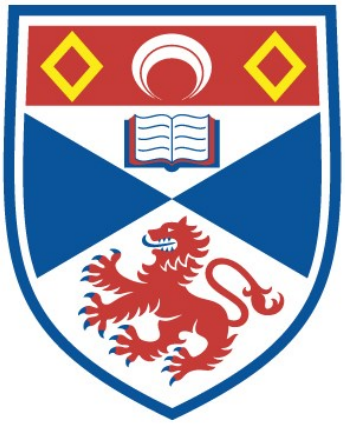
APPROACHES TO FERROCENE-CONTAINING PI-CONJUGATED POLYMERS: (SYNTHESIS, CHARACTERISATION, STRUCTURAL AND ELECTROCHEMICAL STUDIES)

Syed Zaka Ahmed

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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Approaches To Ferrocene-Containing π-Conjugated Polymers

(Synthesis, Characterisation, Structural and Electrochemical Studies)

By

Syed Zaka Ahmed

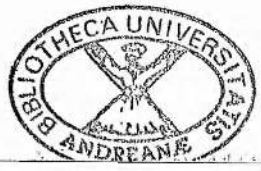
A Thesis presented to the

University of St. Andrews

for the Degree of

Doctor of Philosophy

October 1998



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Dedication

I dedicate this work to my parents,
brothers, sisters,
and my wife Saima & daughter Munibah.

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1. I, *Syed Zaka Ahmed*, hereby certify that this thesis, which is approximately *57,000* words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

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ABSTRACT

The aim of the work carried out for this thesis was to explore ways to synthesise and characterise π-conjugated ferrocene containing polymers by using a condensation polymerization technique. Three types of such compounds were investigated: namely polyquinoxalines (PQx)s, polyimines (PI)s and polyketones (PK)s

The work was started by carrying out the same reactions on small molecules, in order to understand the reaction pathway and to establish the reaction conditions and to obtain the benchmark characterisation data. Initially monofunctional ferrocene derivatives were prepared and condensed with mono- and bi-functional organic molecules, and bifunctional ferrocene derivatives were synthesised and condensed with mono functional organic molecules, to yield the small molecular condensation products. When the reaction conditions had been optimised the same reactions were extended to bifunctional ferrocene derivatives and bifunctional organic entities to obtain the co-polymers.

After citing the relevant references in chapter one, the synthesis of mono- and bi-functional ferrocene containing diketones (FcCOCOR) by the oxidation of the synthesised mono-ketones is described in chapter 2 and their condensation with unsubstituted and substituted organic di-

and tetra-amines to produce ferrocene containing mono-, bis- and poly-quinoxalines is described in chapter 3. The crystal structures of some of the compounds are also determined as definitive proof of characterisation. The attempted oxidation of ferrocenyl monoketones ($FcCH_2COR$) to diketones by using selenium dioxide produced the coupled, dimeric, products $(FcCHCOR)_2$. Electrochemical studies of the synthesised quinoxalines were also carried out.

In chapter 4 are described the condensation of ferrocene aldehyde ($FcCHO$) and dialdehyde [$Fcd(CHO)_2$] with aromatic amines to yield ferrocene containing mono-, bis- and poly-imines. Chapter 5 deals with the synthesis and characterisation of ferrocene containing mono-, bis- and poly ketones synthesised by Friedel Crafts acylation reactions. The molecular weights of the synthesised ferrocene-containing polymers are also estimated with the help of ^1H NMR spectra.

List of Abbreviations

biPh	biphenyl, C_6H_5-C_6H_4- or -C_6H_4-C_6H_4-
b.p.	boiling point
Cp	Cyclopentadienyl anion, $C_5H_5^-$
CP-MAS	Cross Polarization Magic Angle Spining
DMAc	*N,N*-dimethylacetamide
DMF	Dimethyl Formamide
DNA	Deoxyribonucleic Acid
DSC	Differential Scanning Calorimetry
Fc	Ferrocenyl group, (η^5–C_5H_5) Fe (η^5–C_5H_4)
Fcd	Ferrocendiyl group, Fe (η^5–C_5H_4)$_2$
FAB	Fast Atom Bombartment
FCPI	Ferrocene Containing Polyimines
FCPK	Ferrocene Containing Polyketones
FCPQx	Ferrocene Containing Polyquinoxalines
FTIR	Fourier Transform Infrared
HOMO	Highest Occupied Molecular Orbital
ISI	Institute for Scientific Information
LED	Light Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
M	molarity, mol dm^{-3}
m.p.	melting point
NLO	Non Linear Optics or Optical
NMR	Nuclear Magnatic Resonance
Ph	Phenyl group, C_6H_5-
PEEK	Polyetheretherketone

PEK	Polyetherketone
PK	Polyketone
PQx	Polyquinoxaline
PTSA	*p*-Toluenesulfonic acid
R	*rectus*, symbol for right handed carbon atom according to Cahn-Ingold-Prelog system.
Rac or rac	Racemic
S	*sinister*, symbol for left handed carbon atom according to Cahn-Ingold-Prelog system.
T_g	Glass transition temperature of a polymer
T_m	Melting temperature of a crystalline polymer
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMEDA	Tetramethylethylenediamine

List of Compounds

Comp. No.	Name
1	Dicyclopentadienyl iron, showing the sigma bond between the Cp rings and iron atom.
2	Dicyclopentadienyl iron, showing the ionic bond between the Cp rings and iron^{+2} ion.
3	Ferrocene, showing sandwich shape structure.
4	Metallocene, general structure.
5	Decamethyl ferrocene.
6	2-Ferrocenylquinoxaline.
7	2-Ferrocenyl-3-phenylquinoxaline.
8	Ferrocenyl-substitutedphenyl ketimine.
9	Bis(4-iminoferrocenyl-3-methylphenylene-1-yl).
10	2,5,19,22-Tetraaza[6.6](1,1')ferrocenophane-1,5-diene
11	1,1'-(2,6-Diazahepta-1,6-diene)ferrocene
12	Ferrocenylalkyl-disubstitutedphenylimine.
13	Acylferrocene
14	Diacylferrocene
15	Polyquinoxaline repeating unit
16	Polyquinoxaline repeating unit with spacers
17	Polyimine repeating unit
18	Polyketone repeating unit
19	Vinyl ferrocene
20	1,1'-Diisopropenylferrocene
21	α-Hydroxyisopropylferrocene
22	Isopropylferrocene cation
23	Polyisopropylferrocene

24	1,1'-Bis(2-aminoethyl)ferrocene
25	1,1'-Bis(2-hydroxyethyl)ferrocene
26	Ferrocenylsilane
27	Ferrocenylsilane polymer
28	1,1'-Bis(chlorocarbonyl)ferrocene
29	Methylhydroquinone
30	A ferrocene-containing liquid-crystal polymer
31	Formaldehyde
32	Dimethylamine
33	*N,N,N',N'*- Tetramethyldiaminomethane
34	*N,N*-Dimethylaminomethylferrocene
35	(Ferrocenylmethyl)trimethylammonium iodide
36	(Ferrocenylmethyl)triphenylphosphonium iodide
37	(Ferrocenylmethylene)triphenylphosphorane
38	(α-Ferrocenyl-acyl)triphenylphosphonium iodide
38a	(α-Ferrocenylphenacyl)triphenylphosphonium iodide
38b	(α-Ferrocenylbiphenacyl)triphenylphosphonium iodide
39	Ferrocenylarylmonoketones
39a	2-Ferrocenyl-1-phenyl-1-ethanone
39b	2-Ferrocenyl-1-biphenyl-1-ethanone
40	Ferrocenyl-aryl-1,2-diketones
40a	Ferrocenylphenylethanedione
40b	Ferrocenylbiphenylethanedione
41	1-Ferrocenyl-2-phenyl-1-ethanone (an acyl ferrocene)
42a	2,3-Diferrocenyl-1,4-diphenylbutane-1,4-dione
42b	2,3-Diferrocenyl-1,4-bis(biphenyl)butane-1,4-dione
43	Ferrocenecarboxaldehyde

44	4,4'-Biphenyldicarboxylic acid
45	4,4'-Biphenyldicarbonyl chloride
46	4,4'-Dicarbonylbis[ferrocenylmethyl(triphenyl-phosphonium iodide)]
47	1,1-Bis(phenylacetyl)ferrocene
48	Ferrocene-1,1'-diylbis(phenylethanedione)
49	1,2-Diaminobenzene
50	3,4-Diaminobenzoic acid
51a	2-Ferrocenyl-3-phenyl-quinoxalyl-6-carboxylic acid
51b	3-Ferrocenyl-2-phenylquinoxalyl-6-carboxylic acid
52	4-Nitro-1,2-diaminobenzene
53a	3-Ferrocenyl-2-phenyl-6-nitroquinoxaline
53b	2-Ferrocenyl-3-phenyl-6-nitroquinoxaline
54	2,3-Diaminotoluene
55a	3-Ferrocenyl-2-phenyl-5-methylquinoxaline
55b	2-Ferrocenyl-3-phenyl-5-methylquinoxaline
56	2,3-Diaminopyridine
57a	2-Ferrocenyl-3-phenyl-5-azaquinoxaline
57b	3-Ferrocenyl-2-phenyl-5-azaquinoxaline
58	3,3',4,4'-Biphenyltetramine
59a	2,2'-Diferrocenyl-3,3'-diphenyl-6,6'-diquinoxaline
59b	2,2'-Diphenyl-3,3'-diferrocenyl-6,6'-diquinoxaline
59c	2,3'-Diferrocenyl-3,2'-diphenyl-6,6'-diquinoxaline
60	Ferrocenyl-phenyl-6-(3',4'-diaminophenyl)quinoxaline
61	1,1'-Bis(3-phenyl-2-quinoxalyl)ferrocene
62	Repeating unit of ferrocene-containing polyquinoxaline
63	3-Methylaminobenzene
64	*N*-3-methylbenzeneiminomethylferrocene

65	4-Methylamino-benzene
66	*N*-4-methylbenzeneiminomethyl-ferrocene
67	1,4-Diaminobenzene
68	1,4-Benzene-*N,N'*-bis(iminomethylferrocene)
69	*N*-Ferrocenyl-methyl-2-ferrocenylbenzimidazol
70	2-Ferrocenylbenzimidazol
71	1,2-Benzene-*N,N'*-bis(iminomethylferrocene)
72	1,1'-Ferrocenedicarboxaldehyde
73	Repeating unit of ferrocene-containing polyimine
74	Ferrocene-containing tetraimine macrocycle
75	Ferrocene-containing bisimine macrocycle
76	4-Ferrocenylketone-4'-biphenylcarbonylchloride
77	4,4'-Biphenyl-bis(ferrocenylketone)
78	1,4-Benzenedicarbonylchloride
79	1,3-Benzenedicarbonylchloride
80	1-Carbonylchloride-4-ferrocenylketonebenzene
81	1-Ferrocenylketone-3-carbonylchloridebenzene
82	1,3-Benzene-bis-(ferrocenylketone)
83	1,3,5-Benzenetricarbonylchloride
84	1,3,5-Benzene-tris(ferrocenylketone)
85	Repeating unit of ferrocene-containing polyketone
86	Ferrocene-containing tetraketone macrocycle
87	Repeating unit of ferrocene-containing polyketone
88	Ferrocene-Containing tetraketone macrocycle
89	Ferrocene-containing diketone macrocycle.

CHAPTER 1

INTRODUCTION

In this chapter a brief account of the discovery and characterisation, and some common reactions of ferrocene are described. Later in this chapter a literature reference to the organic and ferrocenyl 'quinoxalinic', 'iminic' and 'ketonic' compounds has been provided, references are also cited from π-conjugated aromatic polymers and ferrocene-containing polymers. The aims of the research are also described.

1.1 LITERATURE SURVEY

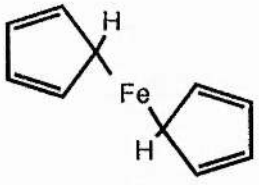
1.1.1 Chronicle of Ferrocene.

The field of *organometallic chemistry* is relatively new, although the initial organometallic compounds were synthesised and to some degree characterised in the 19th century. The first of these was an ethene complex of platinum(II) synthesised by Zeise[1] in 1827. The next major discovery was the first binary metal carbonyl complex by Mond in 1890, who reported the synthesis of nickel tetracarbonyl complex.[2] That followed a substantial amount of research on metal carbonyls during the first half of the 20th century. From a more practical point of view Grignard's Nobel Prize winning synthesis and exploitation of organomagnesium halides[3] provided easily handleable and versatile intermediate for a variety of organic and organometallic syntheses.

However, the rebirth of *Organometallic Chemistry* was the accidental discovery and then characterisation of ferrocene in the middle of the 20th century, that transformed the field of organometallic chemistry into a fast expanding and growing area of research. Now organometallic compounds have paved the way in catalysis, organic synthesis, medicines, agrochemicals, charge transfer complexes, fire retardents, organometallic polymers and materials.

Ferrocene was discovered in 1951 when two independent groups of scientists, almost at the same time, independently reported the same compound prepared from different routes. Miller, Tebboth and Tremaine[4] who were trying to synthesise amines from olefins (cyclopentadiene) and

nitrogen in the presence of iron catalysts and oxides of aluminium, potassium or molybdenum, reported the formation of orange crystals that analysed as $C_{10}H_{10}Fe$. Kealy and Pauson[5] also obtained the same compound in an attempt to oxidise cyclopentadienylmagnesium bromide to fulvalene with anhydrous iron(III) chloride in ether-benzene solution. The new compound was found to be stable and sublimable, and melted at 173° C with excellent solubility in organic solvents but insoluble in water. By analogy to main-group metal alkyls, known at that time, the suggested structure for the bicyclopentadienyliron featured two flat planar cyclopentadienide rings where one of the five carbon atoms of each ring was linked by a single metal-carbon σ (i.e. monohapto η^1) bond **1**. Another structure postulated at that time indicated a divalent iron moiety (Fe^{++}) co-ordinated to two molecules of cyclopentadienyl anions (Cp^-) **2**. However, it was noticed that the new compound was exceptionally stable towards exposure to air, moisture or heat in contrast to other known transition metal alkyl complexes.



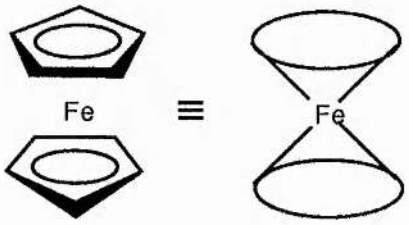
(1)

$[C_5H_5^- Fe^{2+} C_5H_5^-]$

(2)

The true nature of this product was recognised independently by G. Wilkinson[6] at Harvard and E.O. Fischer[7] in Munich; Wilkinson used chemical, physical and spectroscopic methods to elucidate the correct structure of bicyclopentadienyliron, postulating a 'sandwich' shape structure **3a** on the basis of the data while Fischer used X-ray crystallography to structurally characterise the compound, and the X-ray diffraction studies gave unequivocal evidence of the 'sandwich' structure

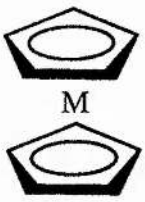
or the 'double-cone' structure **3c**. The iron atom was located between the two planar cyclopentadienyl rings and all the five carbons of *Cp* ring were equally involved in bonding with the central metal atom [η^5-(C_5H_5)Feη^5-(C_5H_5)] **3a, 3c**. The Fischer group then went on to synthesise and carry out crystal structure determinations of other analogues i.e. sandwich compounds involving cobalt, nickel and osmium[8] and demonstrated that this type of structure was not unique to iron. G. Wilkinson and E.O. Fischer were awarded Nobel Prize[9] in chemistry (in 1973) for their pioneering work in organometallic chemistry.



(3a) **(3c)**

In recognition that this new compound, bicyclopentadienyl iron, behaves much like a three dimensional arene, the term '**Ferrocene**' was coined for this compound by Woodward and co-workers.[10] This discovery initiated a boom in transition-metal organometallic chemistry research and in a very short period of time a whole series of bicyclopentadienyl metal complexes having Ni, Co, Cr, Mn, Ru and Os as the central metal atom with general formula (η^5-C_5H_5)$_2$M **4** was prepared;[8,11] by analogy these are known as '**Metallocenes**'. In metallocenes both the *Cp* groups act as a pentahapto (η^5) ligand i.e. all the five carbons of the *Cp* ring are equally involved in bonding with central metal atom. This favourable metallocene structure frequently

overrides the requirement of the *18-electron rule*; first row metallocenes (V-Ni) exist with electron counts from 15 to 20.



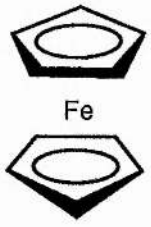
(4)

Soon after the first synthesis of ferrocene, several new and simplified methods were discovered other than the Grignard reagent (cyclopentadienylmagnesium bromide) method. These methods employed alkali metal salts[12-20] (preferably lithium, sodium and potassium) of cyclopentadiene with anhydrous transition metal nitrates or thiocyanates, or ammonium salts[21,22] of cyclopentadiene with iron(II) chloride. The patent literature abounds with variations of this technique for the syntheses of ferrocene in ether,[13-16] ethylene glycoldimethyl ether,[17] tetrahydrofuran,[18] benzene or toluene,[14,15] ethanol[19] and liquid paraffin.[15,20] Both iron(III) and iron(II) salts have been used, although the latter give higher yields since part of cyclopentadienide is not consumed in reduction of the metal salt.[23] Some other cyclopentadienyl complexes, namely bicyclopentadienyl magnesium[24a] and bicyclopentadienyl manganese,[24b] possessing ferrocene-like molecular structures were converted instantaneously and quantitatively to ferrocene with iron(II) chloride. Bicyclopentadienyl compounds of chromium and vanadium yield ferrocene in moderate yield on treatment with iron(II) chloride.[24b]

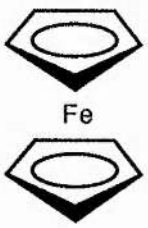
1.1.2 Structure of Ferrocene.

The structure of the ferrocene molecule has also been a matter of attention and debate for some time. In the very beginning, a σ-bond between *Cp* and Fe was postulated that was soon rejected and a more appropriate and acceptable 'sandwich shape' structure was confirmed on the bases of physical and chemical evidence and X-ray crystallography.[6,7] But even after the establishment of the 'sandwich' structure, curiosity did not fade; now the interest was in the conformation of the two *Cp* rings. The original X-ray diffraction studies by Fischer[7] suggested the conformation of the two cyclopentadiene rings in the molecule to be staggered **3a** (D_{5d} symmetry) with a molecular center of symmetry. But now it is known[9] that ferrocene can exist in ordered and disordered phases and possesses interesting structural variations depending on the phase i.e. it can crystallize in monoclinic, triclinic and orthorhombic modifications. The gas-phase electron diffraction studies by Haaland[25] demonstrated the eclipsed conformation **3b** (D_{5h} symmetry). More recent results[9] for the crystals indicate that below the Λ-point transition at 164 K, the triclinic form persists and the configuration is ordered with a D_5 structure with only a 9° rotation from eclipsed (D_{5h}) conformation. The room-temperature monoclinic crystalline form is a disordered species indicating a staggered (D_{5d}) conformation, whilst in the orthorhombic form (T<110 K) the rings are fully eclipsed (D_{5h}). Theoretical studies have shown that for ferrocene the eclipsed form is slightly more stable than the staggered form by 2.78 kJ mole^{-1}. Experimental evidence has confirmed a very low rotation barrier (3.8 kJ mol^{-1}) leading to the possible adoption of either staggered or eclipsed conformation.[9]

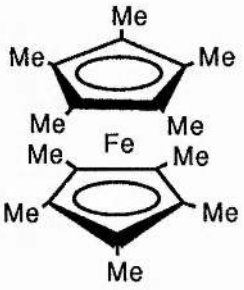
It is interesting to note here that in the gas phase and in the crystal structure $(\eta^5\text{-}C_5Me_5)_2Fe$ **5** adopts a regular D_{5d} conformation with the staggered form 4.2 kJ mol^{-1} more stable than the eclipsed form,[9] presumably due to repulsion between the methyl groups in the opposite *Cp* rings. Mono and 1,1'-bis substituted ferrocene compounds are also usually eclipsed; all the mono- or bis-substituted compounds synthesised and characterised by single crystal X-ray crystallography, at room temperature, in the course of this work also reveal the almost eclipsed conformation of the two *Cp* rings in the substituted ferrocene.



(3a)
(Staggered)



(3b)
(Eclipsed)



(5)
(Staggered)

The other two group 8 analogues of ferrocene, namely Ruthenocene $(\eta^5\text{-}C_5H_5)_2Ru$ and Osmocene $(\eta^5\text{-}C_5H_5)_2Os$ **4** (with M = Ru and Os respectively) are isomorphous with each other with the two *Cp* rings having an eclipsed conformation (D_{5h}). This contrasts with ferrocene which shows a staggered conformation at room temperature, although it is similar to the orthorhombic form and gas phase electron diffraction investigation of ferrocene that show eclipsed conformations. This is clearly because there is greater interannular distance in these metallocenes of group 8 as compared to ferrocene (0.371 nm in osmocene *cf.* 0.332 nm in ferrocene),[9] that reduces the repulsive forces between the *Cp* rings.

1.1.3 Bonding in Ferrocene.

A cyclopentadienyl ligand has five molecular orbitals available for interaction with metal orbitals of suitable symmetry. *Fig. 1* shows a qualitative bonding scheme for ferrocene[26]. Iron-cyclopentadiene bonding

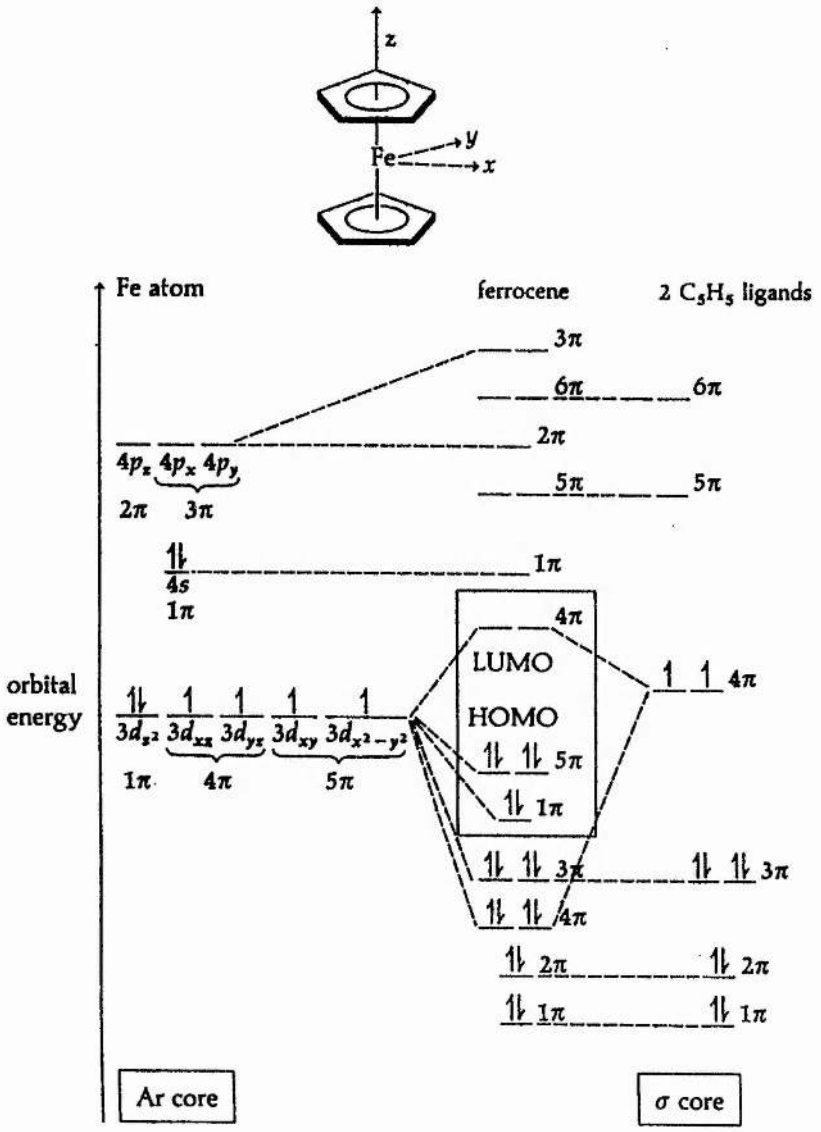


Figure 1.1: A qualitative bonding scheme for $(\eta^5\text{-}C_5H_5)_2Fe$
(adapted from reference 26)

results from π interaction between the ten pπ atomic orbitals of two Cp ligands and *3d, 4s* and *4p* atomic orbitals of iron atom. The orbitals that have the same symmetry, good spatial overlap and similar energies interact strongly. Different possible combinations of the ten $2p_z$ atomic orbitals of the Cp ligands are denoted as 1π, 2π, 3π, 4π, 5π, and 6π, sometimes also named as a_{1g}, a_{1u}, e_{1g}, e_{1u}, e_{2g} and e_{2u} ; each iron valence atomic orbital is also classified as having one of these symmetry types. When iron and Cp ligand orbitals interact they yield the molecular orbitals of ferrocene, shown in the centre of *Fig.1*. The HOMO and LUMO in this figure have essentially *d*-character.

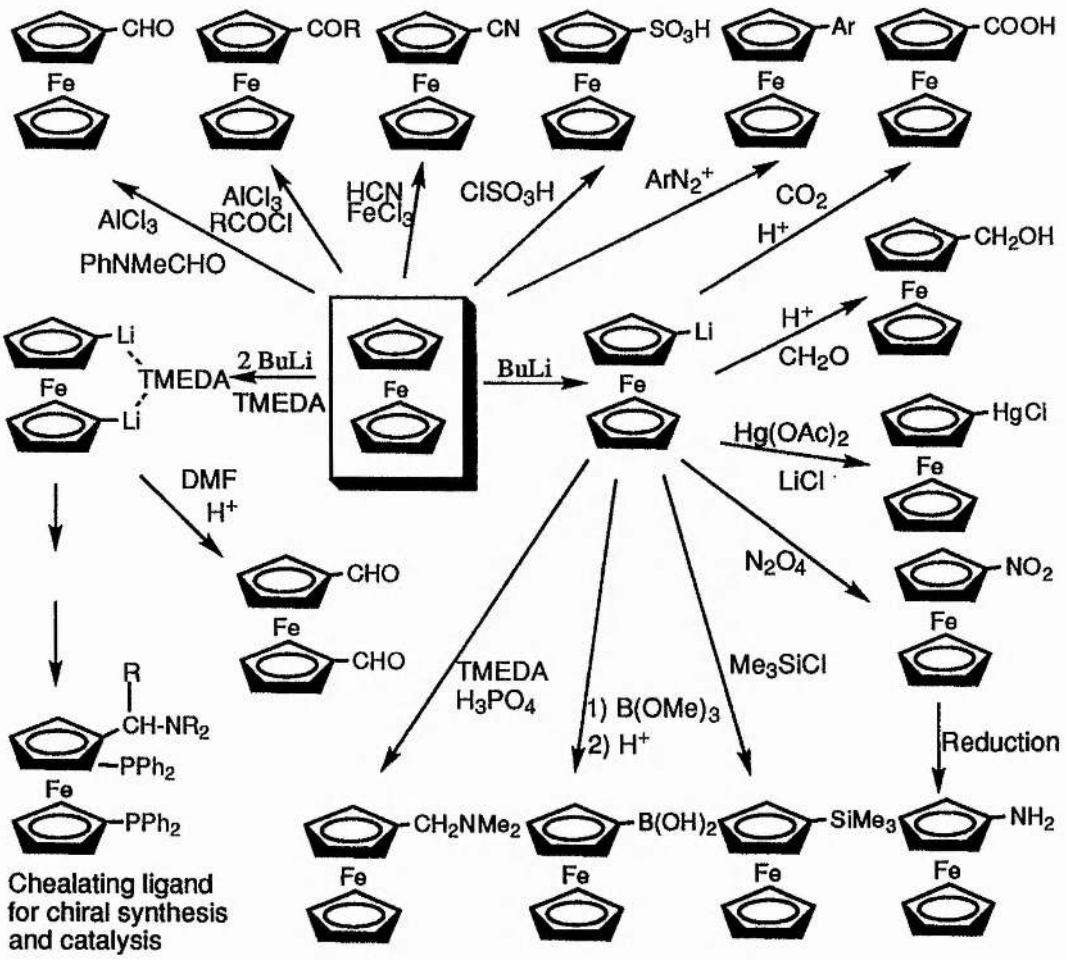
1.1.4 Chemistry of Ferrocene.

Ferrocene is the most stable and perhaps the most well documented member of the metallocene series. It is very stable towards the attack of air, moisture, and most acids and bases. The cyclopentadienyl rings in ferrocene have essentially aromatic character and behave much like electron-rich arenes. Most of the chemistry of ferrocene and its derivatives can be predicted on this basis. Ferrocene can undergo Friedel Crafts acylation,[27] sulfonation and metallation by butyllithium.[28] In Friedel-Crafts acylation it reacts about three million times faster than benzene.[9] The effects of ring substituents on ferrocene have been reviewed by Slocum and Ernst.[29] Introduction of an electron-donating substituent activates the molecule towards electrophilic substitution, preferably at the 1'-position, whereas an electron-withdrawing substituent has the opposite effect. It is interesting to note here that as substitution on one ring has its effect on the substitution of the other ring, this means that

some electronic effect must be passed from one ring to the other through iron.

The ferrocenyl group is one of the strongest inductive electron-releasing agents; this is emphasised by the fact that aminoferrocene is found to be a stronger base than aniline by a factor of 20, while ferrocenecarboxylic acid is a weaker acid than benzoic acid. Ferrocene can be oxidised reversibly, either electrochemically or by oxidising agents such as iodine (and reduced back by common reducing agents such as sodium hydrogen sulfite or ascorbic acid), to give the green-blue paramagnetic ferricenium or ferrocenium cation Cp_2Fe^+. The standard electrode potential of Cp_2Fe/Cp_2Fe^+ in dichloromethane is 0.56V. The Cp_2Fe/Cp_2Fe^+ couple is now used as a standard in cyclovoltametric experiments. A number of ferrocene derivatives are shown in Scheme 1.

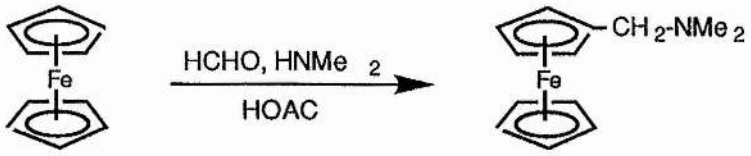
Acknowledging the enormous amount of research on ferrocene and related compounds and exponential increase in ferrocene-containing compounds the *Journal of Organometallic Chemistry* has published an annual review from the mid seventies to the early nineties on this subject.[30] The chemistry of ferrocene is also dealt with on a regular basis in Gmelin's Handbüch.[31] Some of the reactions of ferrocene that are exploited in this thesis are briefly discussed here.



(Scheme 1)

1.1.4.1 Mannich Reaction (Aminomethylation).

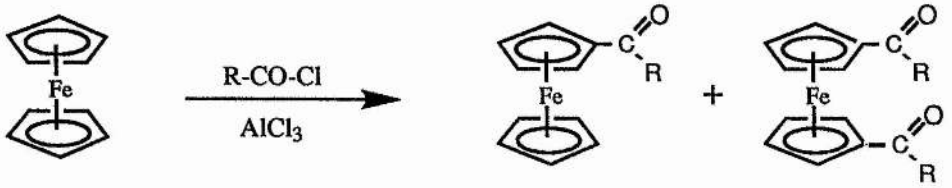
This reaction is demonstrated by reactive aromatic compounds such as phenol and thiophen. In this reaction an aromatic entity condenses with formaldehyde and amine. Benzene does not undergo this reaction; however, ferrocene on condensation with formaldehyde and dimethylamine gives dimethylaminomethylferrocene[32] (Equation 1.1). That can be used in preparation of many ferrocene derivatives. This reaction also demonstrates that ferrocene is more reactive than benzene towards electrophilic substitution.



(1.1)

1.1.4.2 Friedel Crafts Acylation.

The first Friedel Crafts acylation reaction on ferrocene was reported by Woodward *et al.*[10] to demonstrate its aromatic character. In this type of reaction ferrocene is reacted with an acyl chloride in the presence of a Lewis acid such as $AlCl_3$ or $FeCl_3$ (Equation 1.2). Ferrocene undergoes mono-acylation on the first ring about $3x10^6$ times faster than benzene; however Friedel Crafts acylation on the second ring is slower than on the first ring. Acylation on the first ring reduces the reactivity of the second ring towards acylation by a factor of *ca.* $2x10^4$. Both aromatic and aliphatic acylation could be carried out on ferrocene under Friedel Crafts condition.

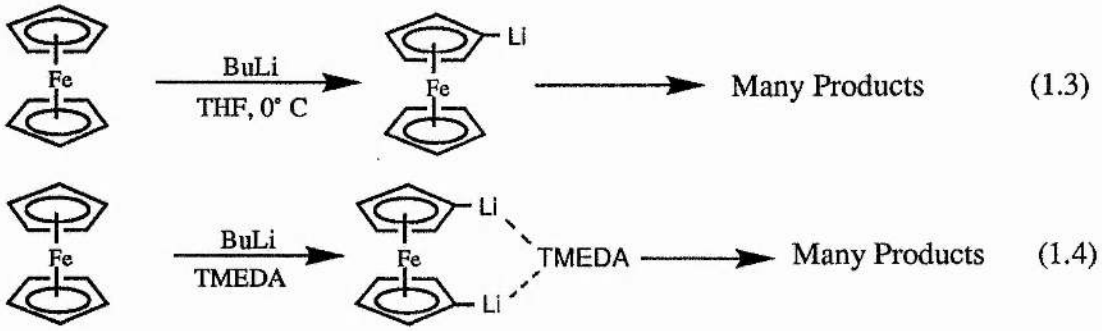


(1.2)

1.1.4.3 Metallation.

Another reaction characteristic of aromatic systems is metallation. A wide variety of compounds has been synthesised by mono[33] or bis lithiation[34] of ferrocene. Monolithiation can be achieved by stoichiometric quantities of n-butyllithium or t-butyllithium in hexane/ether solution. Usually, a yield of about 25-30% is obtained, but use of t-butyllithium in THF at 0° C was reported by Rebiera *et al.*[33b] to improve the yield up to 70% (Equation 1.3). However, the 1,1'-dilithium

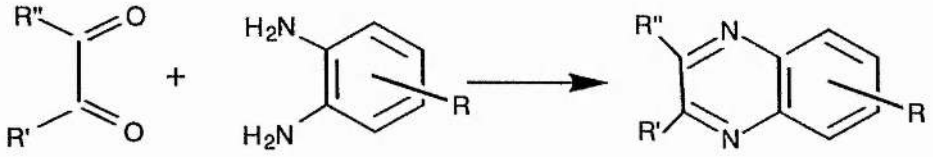
species can be formed exclusively by n-butyllithium with TMEDA[34] (Equation 1.4) The effectiveness of the amine comes from the fact that the lithium atom is strongly complexed with diamine, rendering the organic group even more carbanionic; in addition, the amine breaks down the less reactive RLi tetramer.



1.1.5 Quinoxalines and Ferrocenylquinoxalines.

Quinoxaline is one of the four fused-benzodiazines namely Cinnoline (1,2-diazanapthalene), Quinazoline (1,3-diazanapthalene), Quinoxaline (1,4-diazanapthalene) and Pthalazine (2,3-diazanapthalene). The pK_a of quinoxaline in water at 20° C is 0.56;[35] it is therefore a considerably weaker base than the isomeric diazanapthalenes, it is reported to have a second pK_a of -5.52.[35] The dipole moment of quinoxaline has been reported as 0.51 D in benzene.[35] The nitrogens in the quinoxaline ring can readily be converted to mono- or di- *N*-oxides by electrophilic attack with peracids.[35,36] Quinoxaline itself and many of its derivatives do not readily undergo substitution on carbon when treated with electrophilic reagents; however under vigorous conditions the parent base undergoes an electrophilic substitution reaction. For example acyl radicals (RCO•), generated under oxidizing conditions from aldehydes react with quinoxalines to give ketones; position 2 (sometimes also labelled as α) is

found to be the favoured position for acyl substitution with a range of aliphatic and aromatic aldehydes.[37] The parent quinoxaline also undergoes nitration under forcing conditions to give 5,6-dinitro-quinoxaline as the major product. Electrolytic oxidation of quinoxaline at a copper anode gives pyrazine-2,3-dicarboxylic acid in excellent yield.[38] The later compound has also been synthesised in high yield by oxidation of quinoxaline with alkaline potassium permanganate.[39] Being less reactive for electrophilic substitution reactions, the majority of substituted quinoxalines have been prepared by suitable choice of the reactants in the condensation reaction of primary aromatic *o*-diamines with 1,2-dicarbonyl compounds (Equation 1.5).[35] The dicarbonyl compounds can be diketones or ketoaldehydes, and the aromatic *o*-diamines can be substituted or unsubstituted depending on the structure of the required quinoxaline.

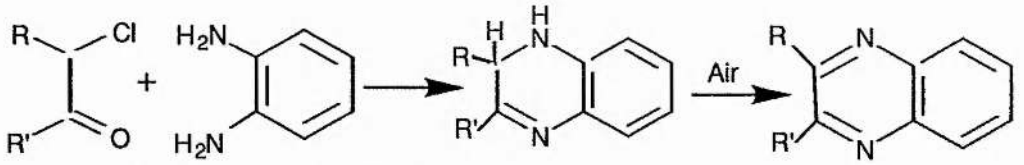


(1.5)

where R, R' and R"= H, Alkyl or Aryl

The condensation reaction invariably proceeds smoothly in alcohol or acetic acid as solvents, but dimethylaniline has also been employed in some cases; condensation may also be accomplished in the melt phase.[40] Quinoxalines can also be synthesised by replacing 1,2-dicarbonyl compounds (diketone or ketoaldehyde) with α-halo carbonyl compounds in the above reaction. This reaction proceeds slowly in hot water or refluxing ethanol.[35] With mono α-halocarbonyl compounds RCHXCOR' a 1,2-dihydroquinoxaline is the unstable primary product which is usually

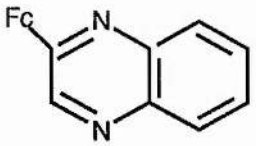
readily oxidised *in situ* by air to the desired quinoxaline[41,42] (Equation 1.6). However, in some cases when the reaction is sluggish, reagents such as iodine, iron(III) salts, benzoquinone and *m*-nitrobenzoic acid are employed to facilitate the oxidation.[35]



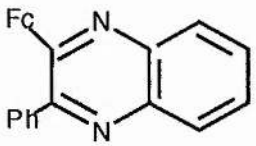
(1.6)

where R, R' = H, Alkyl or Aryl

Syntheses and molecular structures of ferrocene-containing quinoxalines namely 2-ferrocenyl-3-phenylquinoxaline[43] **7** and 2-ferrocenylquinoxaline[44] **6** by employing the procedures above (Equation 1.5 and 1.6 respectively) have been reported by Glidewell *et al.* and Ferguson *et al.*



(6)



(7)

Electrochemical studies of organometallic compounds is one of the hot topics that has generated much of published literature in the last two decades.[45] Several uses of ferrocene-based polymers as biosensors and modified electrodes are discussed by Battaglini *et al.*[45g] in their review beside several other interesting advances in this field. Ferguson, Glidewell and Zanello have investigated the redox behaviour of several ferrocene containing compounds in a series of investigations.[46] Calvo *et al.* have reported that the use of polyallylamine ferrocene-modified electrodes has shown high density currents for amperometric determination of glucose, in agreement with the other published results.[47]

As the quinoxaline moiety exhibits fluorescence and/or phosphorescence behaviour, the substituent effects on the luminescence of 2-substituted-3-methylquinoxalines in poly(vinyl alcohol) films have been reported.[48] This behaviour is also used for quantitative determination of sialic acids in glycoproteins by conversion to a stable fluorescent quinoxaline derivative by the action of *o*-phenylenediamine.[49] Kawakubo, Kato and Iwatsuki[50] have also reported the sensitive fluorimetric detection of copper catalysed aerial oxidation of L-ascorbic acid to dehydroascorbic acid in the presence of *o*-phenylenediamine. Terokubota *et al.* have studied its physical behaviour and reported that the quinoxaline-annelated dimers show excimer type fluorescence and phosphorescence spectra.[51]

Some quinoxaline derivatives have good biological activity and have found their way in pharmacology as well. Curd *et al.*[52] have reported the antimalarial activity of 2,6-dichloro- and 6-substituted-2-chloro-3-dialkylaminoalkylaminoquinoxaline against *plasmodium gallinaceum* in chicks. More recently[53], Woodward *et al.* have carried out *in vitro* studies to investigate the neuroprotective actions of some substituted quinoxalinediones in rat brain.

1.1.6 Ferrocenyl Imines or Schiff's Bases.

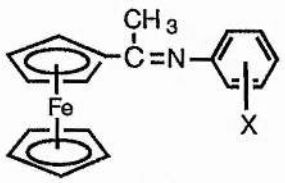
Condensation of a carbonyl group of an aldehyde or a ketone with primary amine in which a double bond between carbon and nitrogen is formed by the elimination of a molecule of water, is a well known and long established reaction (Equation 1.7) The new product is an imine with a C=N functional group. Imines made from ammonia are unstable

and decompose on standing. However if a primary amine is used in place of NH_3 a more stable product is achieved; aromatic aldehydes or amines give most stable imines. These stable imines are also sometimes called Schiff's Bases.

where R, R' = H, aromatic or ferrocenyl compound

Ferrocene-containing imines can be synthesised by the condensation of FcCOR (where R = H, CH_3 or Ph) with an aliphatic or aromatic amine, or alternatively by the condensation of ferrocenyl amine with suitable aldehyde or ketone. This is very interesting to note here that a literature survey on *Science Citation Index* (SCI) of *Institute for Scientific Information Inc.* (ISI) for (ferrocen*+imin*) or (ferrocen*+schiff*) does not produce a single hit prior to 1990 but from 1990 to date the same search produced above hundred hits on this subject and further reactions of the products thereof.

A variety of aromatic and aliphatic amines can be condensed with ferrocene carboxaldehyde, acetyl ferrocene, phenacyl ferrocene and ferrocene dicarboxaldehyde. Huo *et al.*[54] have synthesised ferrocenyl ketimines **8** by condensation of acetyl ferrocene and substituted aminobenzene having substituents at 4- position e.g. OCH_3, Cl, Br, I, and



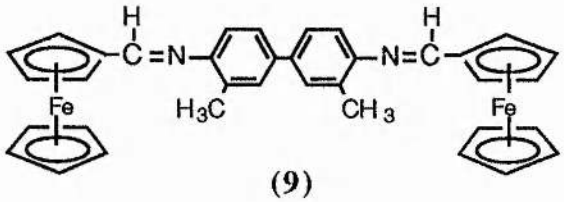
(8)

Where X =
at 4-position OCH_3, Cl, Br, I.
at 3-position CH_3, Cl, Br, NO_2
at 2-position Cl

at 3- position CH_3, Cl, Br, NO_2 and at 2-position Cl and 1 & 2- napthyl amine. They have also studied the cyclopalladated complexes of the above imines. Bosque *et al.* have studied the effect of the substituents on iminic carbon upon the properties of ferrocenylimines and their cyclopalladated complexes.[55] They have synthesised a large variety of novel ferrocenyl-aldimines and ketimines from condensation of phenacylferrocene with aminobenzene, 2-methylaminobenzene, 4-methyl amino benzene, benzylamine, 2-methylbenzylamine and 2-chlorobenzylamine.[55b] Condensation of N,N-dimethylethylenediamine with ferrocene carboxaldehyde was also carried out by them to synthesise a new ferrocenyl schiff base $FcCH{=}NCH_2CH_2N(CH_3)_2$, and this imine was further reacted with transition metal chlorides.[55c] They have summarised and published the results and electrochemical studies of their research on ferrocenylimines synthesised from condensation of ferrocene-carboxaldehyde, acetylferrocene and phenacylferrocene with a variety of aromatic amines; the approach of condensing ferrocenyl amine with aromatic and ferrocene aldehydes was also considered.[56] Solid state reactions of ferrocenyl and ruthenocenyl aldehyde with optically active primary β-hydroxy amines have also been investigated.[57] 2-Amino-benzoic acid, 2-amino-5-methylbenzoic acid and 2-aminonaptholic acid[58] and 4-bromo- and 4-florobenzylamine[59] are also reported to condense with ferrocene carboxaldehyde to yield the corresponding ferrocenylimines, and a crystal structure of a representative compound is also reported.[59]

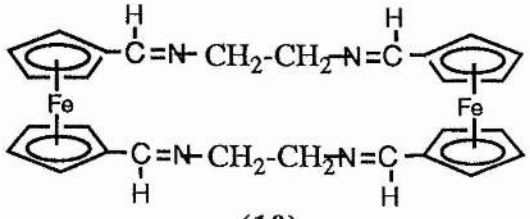
Bisferrocenylbisimines have been prepared by the condensation of ferrocenecarboxaldehyde and aliphatic diamine; ethylenediamine.[60] The

condensation product was reduced to yield parent amine, and copper complex of the amine product has also been reported.[60] Bisferrocenylbisimine has also been synthesised by condensing ferrocene carboxaldehyde with the aromatic diamine, 3,3'-dimethyl-4,4'-diamino-biphenyl[61] to yield bis(4-iminoferrocenyl-3-methylphenylene-1-yl) **9**.



(9)

Tendero *et al.* have synthesised polyazamacrocycles by condensing ferrocenedicarboxaldehyde with ethylenediamine[62a] to yield 2,5,19,22-tetraaza[6.6](1,1')ferrocenophane-1,5-diene **10** and 1,3-propylene-diamine[62b] to yield 1,1'-(2,6-diazahepta-1,6-diene)ferrocene **11**. They have found that in the case of ethylenediamine a dimer is formed i.e. two diamine molecules condensed with two ferrocenedicarboxaldehyde molecules to yield a tetraaza imino macrocycle, while with 1,3-propylenediamine one molecule of diamine condensed with one molecule of ferrocenedicarboxaldehyde to give a diaza imino marcocycle. They have also observed that among the other factors, it would be expected that the distance between the two primary amino groups could determine



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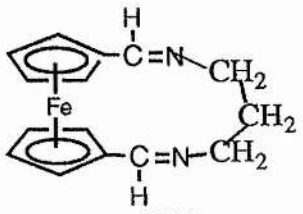
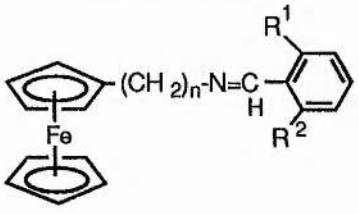


(11)

the nature of final compound i.e. mono or di ferrocene derivative. The parent amine of both imino macrocycles were also reported,[62a, 62b] by $LiAlH_4$ reduction.

The ferrocenylimine, in which ferrocene is directly attached to the nitrogen of imino group, can be synthesised by the condensation of organic aldehyde and amino ferrocene. Bosque *et al.* have reported such ferrocenylimines **12**, by the condensation of aminomethylferrocene[56,64] and aminoethylferrocene[56] with benzaldehyde, 1-chlorobenzaldehyde and 1,6-dichlorobenzaldehyde. Imhof[65] has studies the condensation of ferrocenylamine with thiophen-2-carboxaldehyde and N-methylpyrol-2-carboxaldehyde, to form imines in which ferrocene is directly attached to the nitrogen of imino group. Reactivity of the products with $Fe_2(CO)_9$ was also studied. Lindsell and Xinxin[66] have developed mesogenic ferrocene entities; in this regard they have synthesised some ferrocenenyl aldimines having alkoxy substituents (where alkyl group having 5-9 carbon) on the aromatic amines.



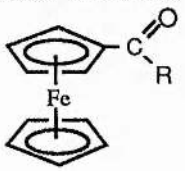
Where n = 1 or 2 and R^1 and R^2 = Cl and/or H)

(12)

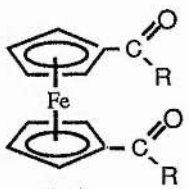
1.1.7 Ferrocenyl Ketones.

Ferrocenyl ketones in which ferrocene is directly attached to the carbonyl carbon were synthesised soon after the discovery of ferrocene. Such compounds **13** can conveniently be produced by Friedel Crafts acylation[10,27] (Equation 1.2; sec. 1.1.4.2) and the literature abounds with

this kind of reaction with ferrocene. Although such a ketone could also be synthesised by MnO_2 oxidation of an alkyl ferrocene,[68] the former method is far more simple and involves readily available chemicals and proceeds smoothly with good yield. Using the right stoichiometric amounts of reagents, the heteroannular diacyl product **14**, having a ketonic function on both rings, can also be obtained[9,33a] under more vigorous conditions than for monoacylation.



(13)



(14)

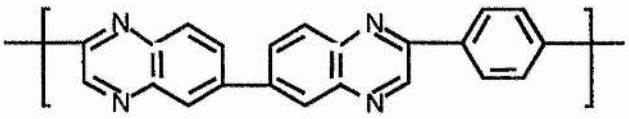
It is generally believed that benzene and its simple analogues behave as monofunctional reagents in Friedel Crafts acylation; acetophenone ($PhCOCH_3$) and benzophenone (PhCOPh) are for example obtained[69] from benzene and the appropriate acyl chloride and diacylation does not apparently occur. It is believed that the deactivating effect of the first acyl group is sufficient to prevent further electrophilic attack on the ring. The above reactions are, however, usually carried out using benzene both as a solvent and a substrate (i.e. in large excess). If benzophenone is allowed to react under Friedel Crafts conditions in excess of benzoyl chloride, at high temperature, the 1,3-disubstituted product *m*-dibenzoylbenzene is produced.[70] *m*-Xylene (1,3-dimethylbenzene),[71] mesitylene (1,3,5-trimethylbenzene)[72] and durene (1,2,4,5-tetramethylbenzene)[72] which are considerably more reactive than benzene towards electrophilic substitution are all reported to yield mixtures of mono- and di-acetyl derivative in 'one-pot' reactions with $AlCl_3$ and excess acetic anhydride.

1.1.8 π-Conjugated Aromatic Polymers.

The preparation of polymers built solely from aromatic fragments has been an object of prime interest, since such a polymer should exhibit excellent thermal stability.[73] One of the major objectives of polymer scientists since the last decade has been high performance engineering thermoplastic polymers, which has, to some extent been achieved e.g. polyarylates, polyetherimides, polyaryl-ether-ketones etc. These are generally characterised by very high heat distortion temperatures and glass transition temperatures (Tg's). One avenue to the fabrication of these materials is via synthesis of new rigid rod type monomers. A polymer having a 'totally aromatic system' may fulfil these criteria. Such a polymer may be synthesised by a polycondensation reaction to provide an aromatic or pseudo-aromatic conjugated system containing one or more hetero atom.

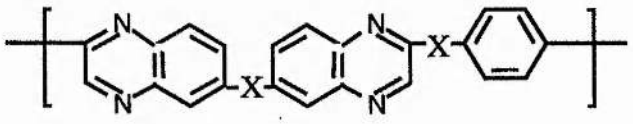
Polyquinoxalines.

One of the reactions that could readily lead to the formation of an aromatic polymer is the formation of the quinoxaline ring by the cyclocondensation of 1,2-dicarbonyl (α-dicarbonyl) compounds with an aromatic 1,2-diamine. The newly formed bond (C=N), in this case, has a very high (6.15×10^5 J/mol) bond formation and hence dissociation energy[35b]. A polymerization reaction utilizing this condensation reaction would require an aromatic tetra amine, in which the amine functions are positioned in two *ortho* sets, and a tetracarbonyl compound in which the ketone or aldehyde groups are situated in two 1,2-dicarbonyl sets joined by an aromatic nucleus. A series of such reactions was carried by Stille *et al.*[74] It is reported that these polymers **15** , having completely conjugated



(15)

aromatic polymer chains, show excellent thermal stability both in air and in nitrogen atmospheres. The temperature at which initial weight loss, in either atmosphere, occurred was nearly 500 °C or above. Unfortunately these polyquinoxalines did not have good physical properties, *i.e.* they were somewhat brittle and insoluble in common organic solvents.[74a,b] Incorporation of flexible groups like ether[74c] (-O-), sulfide[74c] (-S-) and sulfone[74d] ($-SO_2-$), between aromatic and quinoxaline segments, **16**, increased the solubility of the polymer in organic solvents and the flexibility was improved without sacrificing the thermal stability.



where X = O, S, SO_2

(16)

Connel and Hergenrother[75] have synthesised poly(arylene ether)s containing quinoxaline units by the aromatic nucleophilic displacement reaction of novel (phenylquinoxaline) compounds with activated aromatic difluro compounds. The amorphous polymer formed from bis(phenyl-quinoxaline)s had configurational isomers and had Tg 213-283 °C, while the polymer synthesised from bis(phenylquinoxaline)s that did not contain configurational isomers was semicrystalline. The molecular weight of the polymer was limited by its solubility in the reaction medium.

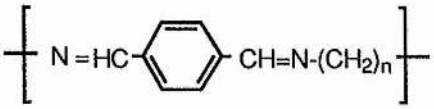
Novel poly(α-diketone)s, having molecular weights up to $2x10^4$, were prepared by Brandukova and Vygodskii[76] by the reaction of different aromatic dicarboxylic acid chlorides and difluorides with SmI_2 in THF at room temperature for 10-20 minutes. Amorphous and heat resistant homo- and copolymers were reported. These polymeric α-diketones were reacted with di- and tetra-amines to form functionalised quinoxalines. This transformation is expected to increase the polymer properties e.g. T_g and T_d, tensile strength and modules. Yamamoto *et al.*[77] have reported the preparation of electron accepting π-conjugated polyquinoxalines (PQx) by dehalogenation polycondensation of 5,8-dibromoquinoxaline derivative and 2,6-dibromoquinoxaline with zerovalent nickel complex. A series of n-conjugated polyquinoxalines with molecular weight $6x10^3$ to $260x10^3$ were reported. The polymers were electrically and chemically reduced and were converted into electrically conducting material with conductivity of $1x10^{-4}$ to $7x10^{-3}$ S cm^{-1}. Poly(quinoxaline-5,8-diyl)s with aromatic substituents exhibit strong fluorescence in solution as well as in cast films. A light emitting diode (LED), ITO/polymer/Mg(Ag) was also reported that emits blue green light at about 500 nm.

Polyimines.

Another approach to the synthesis of totally aromatic polymers having hetero atoms in the polymer back-bone is via the synthesis of polyimines (sometimes also called polyazomethine), by polycondensation of dicarbonyl compounds with the appropriate diamine. The difference between polyquinoxalines and polyimines is that the newly formed C=N bond in the former is incorporated in the aromatic ring while in the later it

synthesised a variety of polyimines by polycondensation of dialdehydes and diamines and have studied both the properties of the resulting polymers and the kinetics of the reaction.[78d]

Natansohn *et al.*[79] have reported a series of semicrystalline polyimines **17** from terepthaldehyde and aliphatic diamines. Cross polarization magic angle spinning (CP-MAS) ^{13}C NMR and thermal behaviour of the polymer **17** were also investigated. Polyimines with short spacers (n = 3 & 4) were obtained only in the elongated *trans* configuration while those having spacers longer than 4 methylene groups allowed the formation of non-planar and a bent *cis* configuration. The *cis* structure, when present, melts first to create an ordered phase which may be semi-crystalline or liquid-crystalline and consists of ordered *trans* structure in a disordered amorphous background. These polyimines form charge transfer complexes with electron acceptor molecules and then the behaviour of the molecule is usually irreversible.[79b] Copolyimines with odd-odd number of methylene units (n = 7 & 9) were also prepared and it was observed that copolyimines show a wider liquid crystalline temperature range than the parent homopolymers.[79b] In another experiment a even-even number of methylene units (n = 8 & 10) copolymer was reported, this polymer exhibits liquid crystalline smectic phase as one of its parent homopolymer with 10 methylene units.[79c]

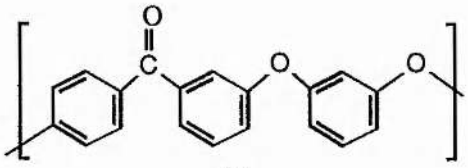


Where n = 3-10 and 12

(17)

Polyketones.

Polyketones (PKs) are usually and commercially synthesised by copolymerization of aliphatic or aromatic olefins and carbon monoxide in the presence of a rhodium or palladium catalyst. Another class of polyketones, polyetherketone (PEK), and polyetheretherketone (PEEK) are commonly synthesised by a simple nucleophilic aromatic substitution between a dihalobenzophenone and a bisphenol. to yield PEEK, **18**.[80] Hendy *et al.*[81] have synthesised a series of polyetheretherketones PEEKs and polyethersulfones PESs. The interest in PKs, PEKs and PEEKs is because of the high polymer properties such as high glass transition temperature T_g, low moisture absorption, high impact strength and tensile strength.



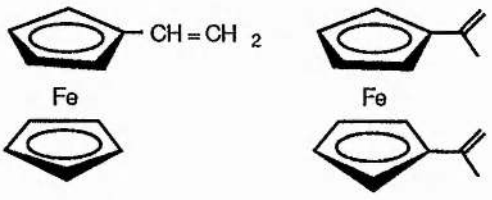
18

Kwiatkowski[82] and co-workers have carried out high molecular weight polymerisation of bisacylchlorides via nickel catalysed coupling in a dry aprotic solvent e.g. DMAc in the presence of triphenyl phosphine or bipyradyl and excess of zinc metal.

Tunca[83] have reported aromatic PEKs with ferrocene in the main chain by direct polycondensation of 1,1'-dicarboxylic acid with biphenylether or 1,4-diphenoxybenzene using various catalysts such as trifluoromethanesulfonic acid (triflic acid), a combination of methylsulfonic acid and P_4O_{10} (Eaten's reagent) or a combination of triflic acid and P_4O_{10}.

1.1.9 Ferrocene Containing Polymers.

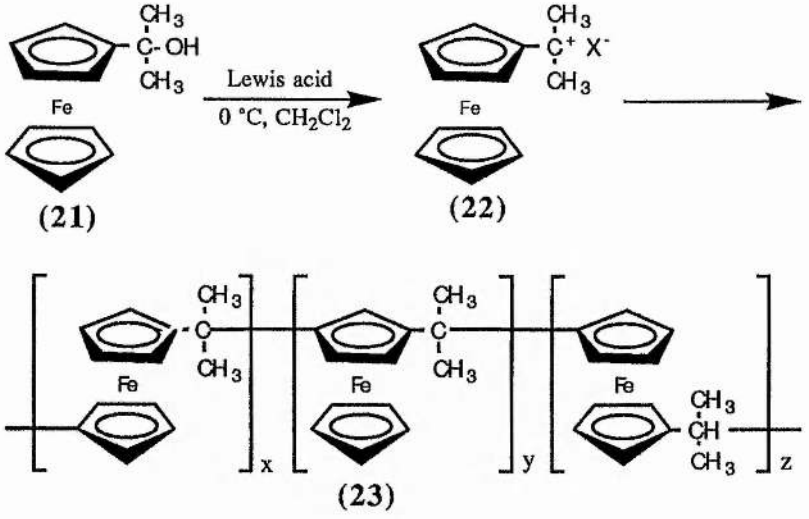
Since its discovery[4,5] ferrocene has intrigued inorganic, organic and polymer chemists. The motivation for incorporating ferrocene in polymer chains is to explore and investigate the potential advantages that metal-containing polymers may have over conventional organic polymers,[84] such as electrical conductivity, magnetic behaviour, thermal stability and non linear optical (NLO) effects. The first organometallic monomer, vinyl ferrocene, **19** was synthesised in 1955, soon after the discovery of ferrocene, by Arimoto and Haven.[86] Its polymerization behaviour was extensively studied by radical,[86,87] cationic[88] and Ziegler-Natta[88] polymerization. It was found to be inert towards the anionic[89] mode of initiation.



(19) **(20)**

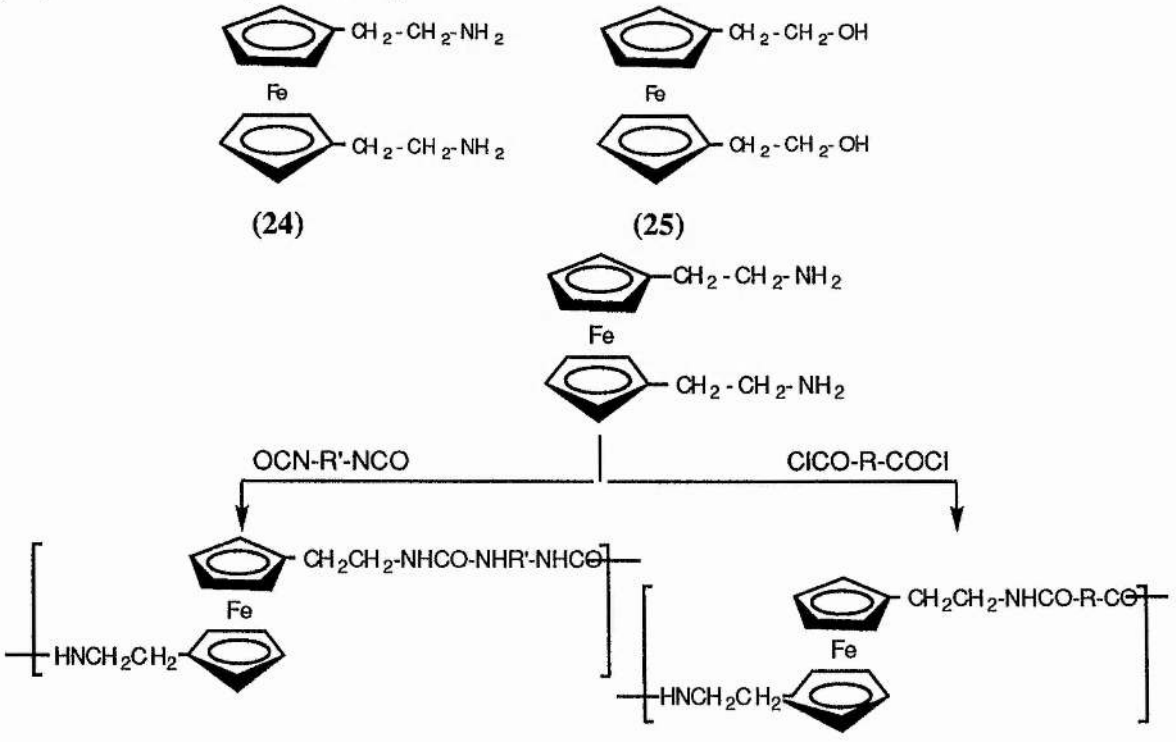
Chisti and Jablonski[90] have reported a low molecular weight oligomer ($8100<M_n<14700$) by homopolymerization of 1,1'-diisopropenylferrocene **20** using $BF_3{\cdot}OEt_2$ and CF_3COOH as initiators at elevated temperature.

The monomer α-hydroxyisopropylferrocene **21** was polymerized at 20 °C using $SnCl_4$ or $BF_3{\cdot}OEt_2$ in dichloromethane for 24-48 h. The polymerization proceeds by self-alkylation of cyclopentadiene ring. The oligomer produced thereby, **23** (scheme 2), contained both homoannular and heteroannular links.[91]



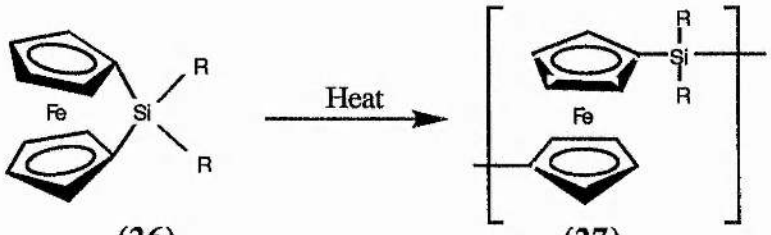
(Scheme 2)

Polycondensation of 1,1'-bis(2-aminoethyl)ferrocene **24** and 1,1'-bis(2-hydroxyethyl)ferrocene **25** has also been carried out with several diacid chlorides and diisocyanates to produce polyesters and polyurethanes[92] (Scheme 3).



(Scheme 3)

Ring-opening polymerization has also been involved in the synthesis of ferrocene-containing polymers. The ferrocenylsilanes[93] and some other analogues[94] are reported to undergo ring-opening polymerization when heated slightly above their melting points (scheme 4). The monomer **26** yielded high molecular weight polymers ($3.2 \times 10^4 < Mn < 4.8 \times 10^5$). These polymers did not exhibit a T_m, the value of T_g depended on the alkyl group substituent and was found to be in the range of -26 to +33 °C.

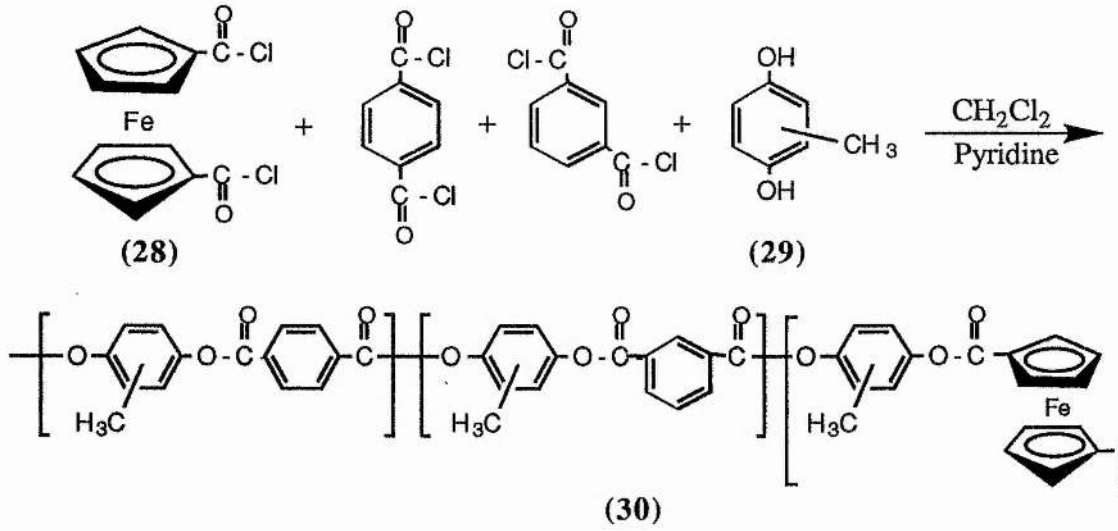


(26) **(27)**

(Scheme 4)

Singh, Raush and Lenz[95] have reported ferrocene-containing liquid crystalline polymers from the solution polymerization of 1,1'-bis(chlorocarbonyl)ferrocene **28**, isophthaloyl chloride, terephthaloyl chloride and methylhydroquinone in refluxing dichloromethane in the presence of pyridine as indicated in Scheme 5. With one exception these ferrocene containing copolyesters were reported to have birefringent melts. The presence of liquid crystallinity was verified by differential scanning calorimetry (DSC), polarized light microscopy and X-ray diffraction studies.

Excellent reviews on ferrocene-containing polymers by Gonsalves and Chen[84] and Neuse[85] may be referred to for a detailed account of this subject.



(Scheme 5)

1.2 AIMS OF THIS WORK.

Among the various branches of polymer science metal-containing polymers have emerged as an important category of polymeric materials. The impetus for developing these materials is based on the premise that metal-containing polymers are expected to possess significantly different properties from those of conventional organic polymers, e.g. electrical conductivity, magnetic behaviour, thermal stability, non-linear optical (NLO) effects, and possibly superconductivity.[84] In recent years a considerable amount of research has been conducted and is being carried out on this group of polymers. Based on the amount of research in this area, it will not be exaggeration to infer that an inter-disciplinary area of research termed *Organometallic Polymer Science* has been established that crosses the conventional boundaries of inorganic, organic, physical and polymer chemistry and material science.[96]

In general there are two basic avenues for the synthesis of metal-containing polymers. One approach is to form derivatives of the existing

organic polymers with organometallic groups. The other involves synthesis of organometallic compounds that contain polymerizable functional groups, these organometallic monomers can then be homo- or co-polymerized with conventional organic monomers. In this work the later approach has been followed .

The aim of the work in this thesis is to synthesise and characterise such ferrocene-containing monomers, these ferrocene containing monomers are bi-functional ferrocene derivatives, that could be polymerized or co-polymerized with appropriate organic monomers to yield π-conjugated aromatic polymers. The copolymerization of these monomers with standard organic monomers is also carried out to yield respective polymers, condensation polymerisation technique is used in this work to synthesise *π-conjugated aromatic ferrocene-containing polymers*. In order to understand the reaction pathway and to establish the reaction conditions and to get the benchmark characterisation data, at the first step monofunctional ferrocene derivatives were prepared and condensed with mono and bifunctional organic molecules, and bifunctional ferrocene derivatives were synthesised and condensed with mono functional organic molecules, to yield the small molecular condensation products. When the reaction conditions were set, the same reactions were extended to bifunctional ferrocene derivatives and bifunctional organic entities to get the co-polymers.

Three type of products were synthetic targets in this thesis; quinoxalines, imines or Schiffs bases, and ketones, with the main emphasis on quinoxaline compounds.

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CHAPTER 2

FERROCENYL 1,2-DIKETONES

In this chapter the synthesis and characterisation of both monofunctional ferrocenyl-1,2-diketones FcCOCOR and difunctional ferrocendiyl-bis(1,2-diketones) Fcd(COCOR)$_2$, is discussed. These ketones react with aromatic di- and tetra-amines to yield quinoxalines which are discussed in the following chapter. Several approaches to the synthesis and oxidation of ferrocenyl monoketones to diketones have been explored; the use of SeO_2 oxidation resulted in unexpected products. The crystal and molecular structures of the products are also described.

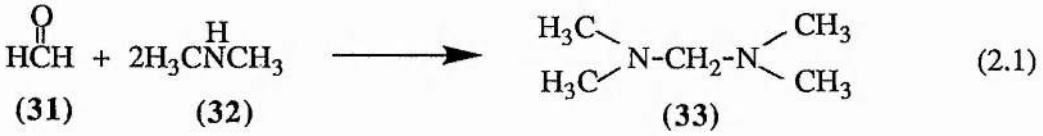
2.1 RESULTS AND DISCUSSION

2.1.1 Monofunctional 1,2-diketones.

Ferrocenyl-1,2-diketones, required for the condensation with aromatic 1,2-diamines in order to make a quinoxaline ring, have been synthesised by the oxidation of ferrocenyl monoketones having a methylene group next to carbonyl carbon. The ferrocenyl monoketones themselves were prepared in a series of reactions starting from simple and readily available chemicals.

2.1.1.1 Steps leading to Ferrocenyl monoketones.

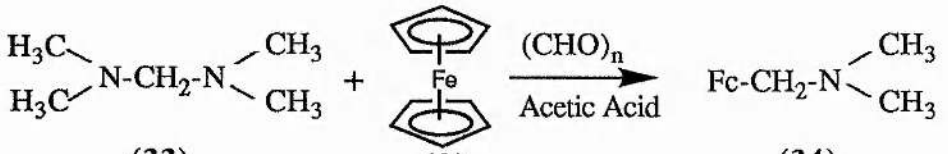
Ferrocenyl monoketones having a methylene (CH_2) group adjacent to carbonyl group have been synthesised starting from formaldehyde, dimethylamine and ferrocene.[1] *N,N,N',N'*- tetramethyldiaminomethane **33** was prepared as a colourless liquid (70% yield) at the first step from the reaction of aqueous formaldehyde **31** and aqueous dimethylamine **32** (Equation 2.1). The compound **33** has very simple ^1H and ^{13}C NMR spectra having two peaks in each of them, one for the methyl and the other for the methylene group.



(31) **(32)** **(33)** (2.1)

The above compound **33** on reaction with ferrocene **3** in the presence of paraformaldehyde and acetic acid (Mannich Reaction)[1] yielded (84%) *N,N*-dimethylaminomethylferrocene **34** (Equation 2.2) as a dark brown oil. The ^1H NMR spectrum of this compound shows the characteristic signature of mono-substituted ferrocenes, three peaks having integration

5:2:2 in the ferrocene region representing one for unsubstituted Cp ring and the other two for the substituted Cp ring in ferrocene, along with two peaks in the alkyl region quite downfield due to the neighbouring ferrocene and nitrogen. The ^{13}C NMR spectrum also shows four peaks in the ferrocene region, characteristic of mono substituted ferrocene, one for unsubstituted Cp ring and three for the substituted ring including one quaternary carbon, in addition to two peaks for the methyl and methylene carbons.



(33) (3) (34) (2.2)

N,N-dimethylaminomethylferrocene **34** on treatment with methyl iodide produced (ferrocenylmethyl)trimethylammonium iodide (90% yield) **35** as a yellow crystalline solid[2,3] (Equation 2.3). ^{1}H and ^{13}C NMR spectra of this compound showed all the expected peaks, and the m.p. of the compound is also in agreement with the literature value.[2]

(34) (35) (2.3)

The trimethylammonium group in **35** was replaced by triphenyl phosphonium group by refluxing **35** with triphenylphosphine in ethanol, (Equation 2.4). Pouring the refluxed mixture into diethyl ether produced **36** in 90% yield as yellow crystalline solid. The change of substituent at the methylene carbon can easily be recognized from the splitting of the CH_2 peak into a doublet due to P-C coupling, both in ^{1}H and ^{13}C NMR spectra. The m.p. was also found to be consistent with the literature value.[4]

$$\underset{\textbf{(35)}}{FcCH_2\overset{+}{N}(CH_3)_3I^-} + PPh_3 \longrightarrow \underset{\textbf{(36)}}{FcCH_2P^+Ph_3I^-} \qquad (2.4)$$

(Ferrocenylmethylene)triphenylphosphorane **37** was prepared by the action of phenyllithium on (ferrocenylmethyl)triphenylphosphonium iodide **36.** Compound **37** was further converted to (α-ferrocenyl-acyl)triphenylphosphonium iodide **38**, in the same pot, by reacting with an acyl chloride (Equation 2.5).[5,6] Compounds of type **38** were obtained as deep red prismatic crystals in 73-83% yield based on **36.**

$$\underset{\textbf{(36)}}{FcCH_2P^+Ph_3I^-} + Ph^-Li^+ \longrightarrow \underset{\textbf{(37)}}{FcCH{=}PPh_3} \xrightarrow{ArCOCl} \underset{\textbf{(38)}}{FcCH(COAr)P^+Ph_3I^-} \qquad (2.5)$$

(a) Ar = Ph (b) Ar = Ph-Ph

As the α-carbon, adjacent to the ferrocene moiety, in **38** is a stereogenic center, so all the five carbons of substituted Cp ring in ferrocene appear at different chemical shifts in the ^{13}C NMR spectrum. P-C coupling is also clear in this case. The single crystal X-ray crystallography of compound **38a** was carried out[5] (section 2.1.1.5.1), confirming that the product, (α-ferrocenylphenacyl)triphenyl-phosphonium iodide, is absolutely free of chloride contamination, although chloride (as benzoyl chloride) was present in the reaction mixture. Appendix I shows that how in this case the iodide salt is the only thermodynamically possible product.

Reduction of **38** with zinc/acetic acid displaced PPh_3 and the ferrocenylmonoketone **39** was obtained:[6] this is a very labile compound which decomposes/oxidises at room temperature (Equation 2.6). ^1H and ^{13}C NMR and elemental analysis of the freshly prepared compound

confirms the composition supported by single crystal X-ray diffraction analysis (section 2.1.1.5.2). The ^{1}H and ^{13}C NMR spectra show the pattern characteristic of monosubsituted ferrocene, together with a CH_2 peak and phenyl peaks; the ^{13}C spectrum also has a ketonic carbonyl resonance.

$$\underset{\textbf{(38)}}{FcCH(COAr)P^{+}Ph_3I^{-}} \xrightarrow{Zn/Acetic\ Acid} \underset{\textbf{(39)}}{FcCH_2COAr} \qquad (2.6)$$

(a) Ar = Ph (b) Ar = Ph-Ph

The acylferrocene, 1-ferrocenyl-2-phenyl-1-ethanone[6] **41**, isomeric with the above ferrocenylarylmonoketones **39**, was also synthesised in a single step reaction by Friedel Crafts acylation of ferrocene (Equation 2.7), a reaction known since the discovery of ferrocene, in 84% yield and was characterised by NMR and on the basis of m.p. The ^{1}H and ^{13}C NMR spectra are similar to those of its isomer **39** with some variations in the peak positions.

$$\underset{\textbf{(3)}}{FcH} + Ph\text{-}CH_2\text{-}CO\text{-}Cl \xrightarrow{AlCl_3} \underset{\textbf{(41)}}{FcCOCH_2Ph} \qquad (2.7)$$

2.1.1.2 Oxidation of ferrocenyl monoketones to 1,2-diketones.

Ferrocenylarylketones **39** were oxidised to corresponding 1,2-diketones **40** by using the well-established synthetic procedure[2,3,6-8] employing manganese dioxide as oxidising agent (Equation 2.8). TLC of the crude reaction mixture shows a red spot corresponding to 1,2-diketone and a yellow spot of lower R_f value indicating ferrocenecarbox-aldehyde (compared with an authentic sample both by TLC and NMR). The yields of 1,2-diketones in this reaction were not very high as cleavage of the bond between CH_2 and CO occurs, giving rise to some

ferrocenecarboxaldehyde **43** concomitantly, regardless of the nature of the aryl group (Ar) . After chromatography over silica gel, dark-red plate-like crystals of **40b** were grown from ethanol; their structure was determined by single crystal X-ray crystallography (section 2.1.1.5.3). The ^{13}C spectrum of compound **40** shows two ketonic resonances along with usual ferrocenyl and phenyl or biphenyl resonances; the ^{1}H spectrum is also easily assignable to the synthesised compound.

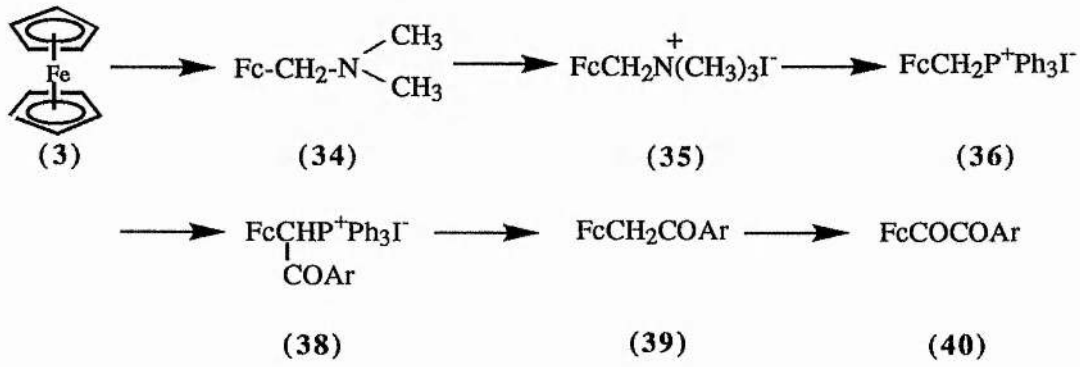
$$\underset{\textbf{(39)}}{FcCH_2COAr} \xrightarrow{MnO_2} \underset{\textbf{(40)}}{FcCOCOAr} + \underset{\textbf{(43)}}{FcCHO} \qquad (2.8)$$

(a) Ar = Ph (b) Ar = Ph-Ph

Bearing in mind that the activity of MnO_2 may have an effect on the yield of the 1,2-diketone, a very active manganese dioxide was synthesised, as reported by Fatiadi in his review,[9] for oxidation as in equation 2.8. However almost the same yields of 1,2-diketones were obtained by using commercially available manganese dioxide from Aldrich and a sample made by the Fatiadi's method. The synthesis of ferrocenyl-1,2-diketones from ferrocene is summarised in scheme 2.1. The structures of compounds **35**, **36**, **38a**, **39b** and **40b** have been confirmed by single crystal X-ray analysis (section 2.1.1.5).

Attempted oxidation of the acyl ferrocene **41** using very active manganese dioxide and commercially available MnO_2 in different solvents led to incomplete reaction even after refluxing for 24 hours in methylcyclohexane. Reflux in 1,1,2-trichloroethane for 48 hours led to a mixture of starting material and diketone **40**. As the ferrocenyl diketone **40** and the acyl ferrocene **41** both have very similar R_f values, it is very

difficult to separate them using column chromatography. The other routes to oxidise acyl ferrocene **41** by using DMSO/HBr,[10] potassium permanganate[6] or titanium molecular sieves (TS-1)[11] failed drastically as the ferrocene moiety itself started oxidative decomposition by these oxidising agents. In the oxidation of ferrocenyl monoketones to diketones the choice of the oxidising agent and the reaction conditions are very crucial because of the sensitivity of ferrocene. The route shown in Scheme 2.1, although lengthy and laborious, yields the pure ferrocenyl diketone **40** required for further reactions with aromatic di- and tetra-amines.



Scheme 2.1

2.1.1.3 Oxidation of ferrocenyl monoketones by selenium dioxide.

Selenium dioxide is another widely used reagent for the oxidation[6-8] of monoketones having a methylene group adjacent to the carbonyl carbon $RCOCH_2R'$, to 1,2-diketones RCOCOR'. However it was reported[6] a long time ago that attempted use of this reagent for the oxidation of ferrocenyl monoketones led to complete decomposition in a variety of solvents, although the solvents used were not specified. The use of selenium dioxide as a possible oxidant for ferrocenylaryl monoketones **39** has now been reinvestigated; in refluxing acetic

anhydride this reagent gives a modest yield of the 1,2-diketone **40** along with a much bigger yield of two less polar coupled products **42** *(Equation 2.9)*. TLC of the oxidised material from each of **39a** and **39b** indicated a red spot for the corresponding diketone in addition to the presence of two less polar yellow products. These yellow products have very similar R_f value in case of **42a** and rather different R_f values for **42b**. In the case of the products from **39a**, only one of the yellow components **42a** could be isolated pure and characterised, but both yellow products from **39b** have been isolated and characterised.

$$\underset{\textbf{(39)}}{\text{Fc-CH}_2\text{-CO-Ar}} \xrightarrow[\text{Acetic Anhydride}]{\text{SeO}_2} \underset{\textbf{(42)}}{\begin{array}{l}\text{Fc-CH-CO-Ar}\\ \quad\quad\text{I}\\ \text{Fc-CH-CO-Ar}\end{array}} + \underset{\textbf{(40)}}{\text{Fc-CO-CO-Ar}} \qquad (2.9)$$

(a) Ar = Ph (b) Ar = Ph-Ph

The ^1H and ^{13}C NMR spectra of compound **42a** both contained signals readily assignable to a mono-substituted ferrocene nucleus and a phenyl ring; in addition there was the expected CO resonance in the ^{13}C spectrum. However, the CH_2 signals for the precursor **39a** were replaced by signals characteristic of a CH group, while the substituted cyclopentadienyl ring of the ferrocene group gave four and five chemical shifts respectively in the ^1H and ^{13}C spectra, indicative of the presence of a neighbouring stereogenic centre rendering all five carbon atoms of this ring chemically and magnetically distinct. The simplest interpretation of these spectral data, in terms of oxidation of $FcCH_2COPh$ to the hydroxyketone FcCH(OH)COPh, was however easily ruled out by the elemental analysis, and by the absence of ν(OH) in the IR spectrum: moreover, the ^1H and ^{13}C chemical shifts of the unique CH group were scarcely consistent with the presence of both OH and CO groups as near-

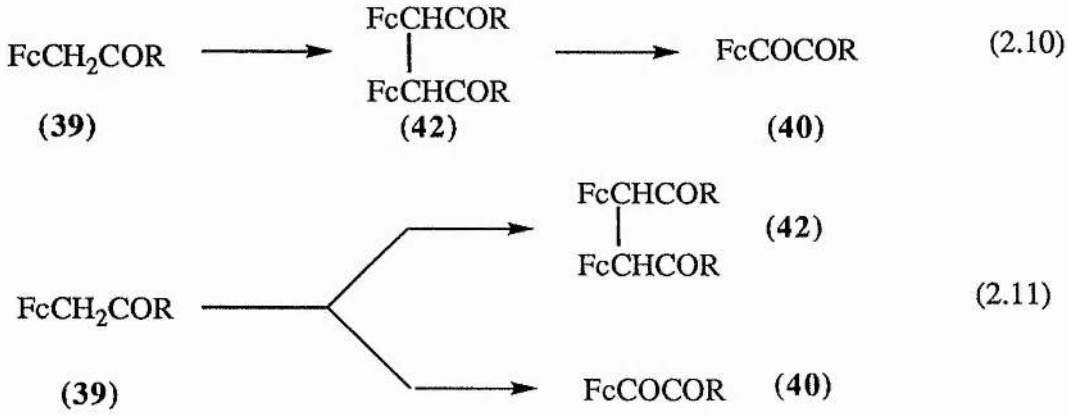
neighbours. The approximate position of a CH group α– to a CO, an OH and an aromatic entity should be around 80 ppm in ^{13}C NMR spectrum. An alternative formulation consistent with all the spectral and analytical data involves an oxidative coupling reaction to give the substituted butane-1,4-dione $(FcCHCOPh)_2$ **42a** in which a new C-C bond has been generated. Single-crystal X-ray diffraction confirms that this formulation is correct, and that the isolated compound is the racemic form consisting of equal numbers of the *RR* and *SS* diastereoisomers (section 2.1.1.5.4).

During the work-up of compound **42a** it was apparent that before the final chromatographic separation each peak in the ^{1}H and ^{13}C NMR spectra was accompanied by a much smaller peak, of very similar chemical shift. Thus the major pattern, identical to that of the pure **42a** used for analytical, spectral and crystallographic characterisation, was mirrored by an entirely similar pattern with much lower intensities: integration of the ^{1}H spectrum indicated a ratio of major to minor components of *ca.* 7:1. While insufficient of this minor component has been isolated for characterisation, a reasonable hypothesis is that this material is in fact the RS (≡ SR) diastereoisomer of **42a**, i.e. the meso form.

The yellow product formed by SeO_2 oxidation of **39b** had ^{1}H and ^{13}C NMR spectra fully consistent with its formulation as **42b**. The crude yellow mixture exhibited a doubling of each signal in the ^{13}C NMR spectrum, rather as for crude **42a**, but with the two components of each signal having intensities in the ratio *ca.* 2:1 as calculated by ^{1}H integration. Separation of this mixture on silica gel gave two pure products, both of which gave crystals suitable for single crystal X-ray

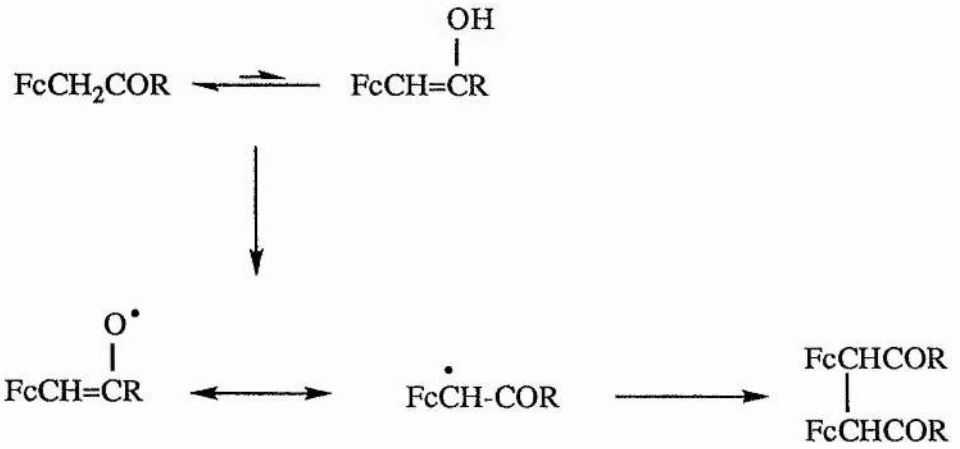
analysis. The less polar and more abundant component proved to be the RR/SS diastereoisomer, denoted *rac*-**42b**, analogous to that characterised earlier for **42a**, and the more polar, less abundant, component proved to be the RS diastereoisomer, denoted *meso*-**42b**. Thus the isolation and structural characterisation of both *rac*-**42b** and *meso*-**42b** rules out any possibility that the observed doublings in the NMR spectra of the crude products could be due to the occurrence of rotamers arising from restricted rotation about the newly-formed C-C bonds, and supports the supposition above that the minor compound accompanying the isolable **42a** is the corresponding meso diastereoisomer.

The formation of the coupled products **42** alongside the expected diketones **40** naturally raises the question of the reaction pathway, and two possibilities present themselves. The coupled products **42** could be intermediates on the pathway from **39** to **40** (Equation 2.10), or alternatively products **40** and **42** could be formed by divergent routes from **39** (Equation 2.11).



In order to test these possibilities, a sample of racemic **42a** was isolated and purified as already described, and then subjected to SeO_2

oxidation under precisely the conditions employed for the oxidation of **39a**. The reaction was monitored by TLC but no **40a** was detected at any stage during a 5 h reaction time: aside from a small amount of decomposition, the **42a** initially added was recovered unchanged. Hence it can be concluded that compounds **40** and **42** do not lie on a common reaction pathway, and that *Equation 2.11* best represents their formation. While the details of the route from **39** to **42** in an oxidation reaction occurring primarily at the surface of the SeO_2 must be somewhat speculative at this stage, a reasonable possibility is the formation by hydrogen abstraction of a radical derived from the enol form of **39**, followed by radical coupling (Equation 2.12).



(2.12)

The formation of the coupled products **42** appears to be specific for SeO_2 oxidations carried out using acetic anhydride as the reaction solvent. When the monoketone **39b** was subjected to SeO_2 oxidation under similar conditions but using either 70% acetic acid or THF as solvent, there was no trace of any **42b** amongst the products: the isolable ferrocene product in each case was the diketone **40b**, in yields of 35% and 10% respectively.

2.1.1.4 Oxidation of other ferrocenyl precursors by selenium dioxide.

Isomeric with the ferrocenyl monoketones **39** are the acyl ferrocenes $FcCOCH_2R$, oxidation of $FcCOCH_2Ph$ **41** to FcCOCOPh **40** using MnO_2 is known to be very slow[6], and its oxidation using SeO_2 proves to be even less effective. No oxidation at all was observed when $FcCOCH_2Ph$ and SeO_2 were heated under reflux in acetic anhydride, glacial acetic acid, or 20% aqueous acetone, although traces of FcCOCOPh were formed in toluene and THF as identified by Tlc compared with authentic sample

However, oxidation of the phosphonium salt $[FcCH(COPh)PPh_3]^+ I^-$ **38a** with SeO_2 in 20% aqueous acetone yielded FcCOCOPh **40a** in 60% yield: this salt was previously used as the precursor to the monoketone **39a** prior to oxidation to **40a** and/or **42a**. It is thus possible to eliminate the reduction of this salt to the labile $FcCH_2COPh$, and to use the salt directly in a more efficient route to the diketone **40a**. Again, the choice of solvent is critical: much poorer yields of **40a** (typically around 10%) were found in neat acetone or in methanol or ethanol, and in each case the diketone was accompanied by a comparable yield of the cleavage product FcCHO **43**; when dichloromethane was chosen as a solvent, this aldehyde was the sole isolable product. Table 2.1 summarises the results of oxidation of various ferrocenyl precursors by using selenium dioxide as oxidant in a variety of solvents.

Table 2.1 The results of oxidation of various ferrocenyl precursors by using selenium dioxide as oxidant in different solvents.

No.	Type of monoketone	Oxidizing agent	Solvent	Product(s)	Yield
1.	$FcCH_2COPh$	SeO_2	Acetic Anhydride	$(FcCHCOPh)_2$ + FcCOCOPh	55% 10%
2.	$FcCH_2CObiPh$*	SeO_2	Acetic Anhydride	$(FcCHCObiPh)_2$ + FcCOCObiPh	69% 13%
3.	$FcCOCH_2Ph$	SeO_2	Acetic Anhydride	No reaction (longer reflux leads to destruction of molecule)	
4.	$FcCOCH_2Ph$	SeO_2	Acetic Acid	No reaction (longer reflux leads to destruction of molecule)	
5.	$FcCH_2CObiPh$*	SeO_2	70% Acetic Acid	FcCOCObiPh	~34%
6.	$FcCOCH_2Ph$	SeO_2	Toluene	FcCOCOPh	traces
7.	$FcCH_2CObiPh$*	SeO_2	THF	FcCOCObiPh	10%
8.	$FcCOCH_2Ph$	SeO_2	THF	FcCOCOPh	<10%
9.	$FcCOCH_2Ph$	SeO_2	20% Aq. Acetone	no reaction	-
10.	$[FcCH(COPh)PPh_3]^+I^-$	SeO_2	20% Aq. Acetone	FcCOCOPh	60%
11.	$[FcCH(COPh)PPh_3]^+I^-$	SeO_2	MeOH/EtOH	FcCHO/FcCOCOPh	12/8%
12.	$[FcCH(COPh)PPh_3]^+I^-$	SeO_2	Acetone	FcCHO/FcCOCOPh	10/10%
13.	$[FcCH(COPh)PPh_3]^+I^-$	SeO_2	CH_2Cl_2	mainly FcCHO	~ 16%

* biPh = $-C_6H_4-C_6H_5$

2.1.1.5 Crystal and Molecular Structures of Ferrocenyl mono- and diketones.

Crystals were grown by slow evaporation of the compounds **38a**, **39b**, **40b**, ***racemic*-42a**, ***racemic*-42b** and ***meso*-42b** and single crystal X-ray crystallography was carried out at room temperature (other than for **39b** which was carried out at 200 K), for structural elucidation and characterisation of the compounds.

2.1.1.5.1 *Crystal and molecular structure of 38a.*

The single-crystal X-ray structure of **38a**, crystallized from aqueous acetone, is shown in Figure 2.1; details of the crystal data can be found in appendix II. This compound crystallizes in the orthorhombic system; space group Pbca was assigned uniquely from the systematic absence. The structure of this compound consist of ion pairs in which there is a single short C-H···I^- interaction involving C62 (Figure 2.1), characterised by C···I^- 3.836(7) Å and C-H···I^- 151°. There are also two further fairly short C-H···I^- interactions involving C44 in the cation at [C···I 3.932(7) Å, C-H···I 134°] and C33 in the cation at [C···I 3.995(7) Å, C-H···I 132°], which serve to generate a continuous network.[5] The cations are chiral, but the space group accommodates equal numbers of *R* and *S* enantiomers, the structure shown in Figure 2.1 represents *R* configuration. The almost perfectly staggered conformation about C1-C2 bond is such that O2 and H1 are antiperiplanar, while O2 and P1 are synclinal. The ferrocene fragment, as usual, has an almost eclipsed conformation, the mean value of the torsion angle C1*i*-Cp1-Cp2-C2*i* (i = 1,2; Cp1 and Cp2 are the ring centroids) is 9.5(4)° and the two Cp rings are only 2.3(4)° from being parallel.

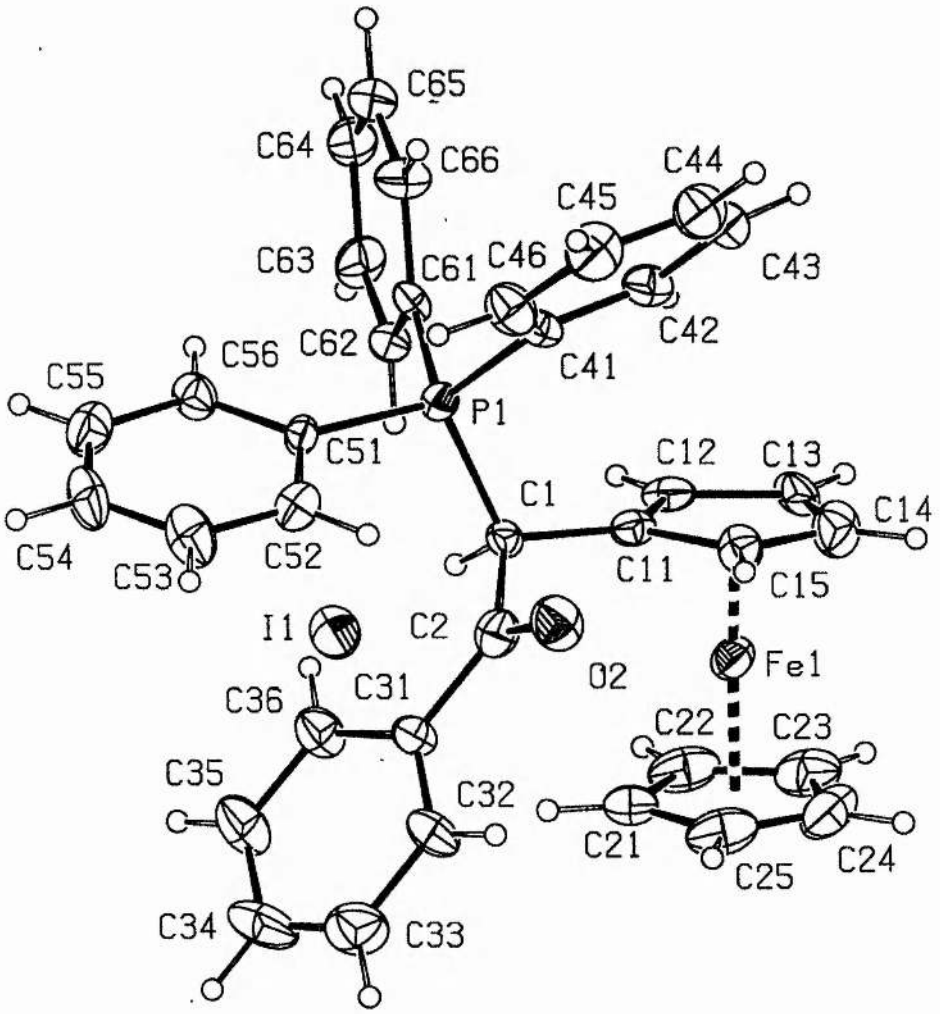


Figure 2.1: Single crystal X-ray structure of (α-ferrocenylphenacyl)triphenylphosphonium iodide ***38a****. The structure above is the R conformer while the space group Pbca accommodates equal numbers of R and S enantiomers.*
(Adapted from reference 5)

2.1.1.5.2 *Crystal and molecular structures of 39b.*

All attempts to grow crystals of **39a** were unsuccessful; however as a result of continued efforts, very thin orange-yellow, plate-like crystals of 2-ferrocenyl-1-biphenyl-1-ethanone **39b** were grown under nitrogen from dichloromethane. The crystal quality was consistently poor and a number of crystals from different preparations were investigated by single crystal X-ray diffraction analysis: the data obtained at 200 K are not of very high quality but probably the best that can be achieved for this compound, but are sufficient to serve as definitive proof of the constitution of this compound;[7] *Figure 2.2* give two views of the molecular structure of this compound, and details of crystallographic data may be seen in appendix III. The compound crystallizes in the monoclinic crystal system, in space group C2/c. The cyclopentadiene rings in ferrocene are almost eclipsed, consistent with other substituted ferrocenes, as is clear from the top view of the molecule, and the fragment C1-C11-C12-C13 is almost *trans* planar. The two phenyl rings are almost in the same plane.

2.1.1.5.3 *Crystal and molecular structures of 40b.*

The ferrocenylbiphenylglyoxal **40b** crystallizes in the orthorhombic crystal system having space group $P2_12_12_1$ with one molecule in asymmetric unit.[6] Within the molecule the acyl fragment is almost coplanar with the substituted cyclopentadienyl ring and the biphenyl group itself is virtually planar. The ferrocene fragment is almost eclipsed as usual. The torsional angle O-C-C-O takes the value 113.3(9)°. The X-ray structure of **40b** is shown in Figure 2.3 and crystallographic details are presented in appendix IV.

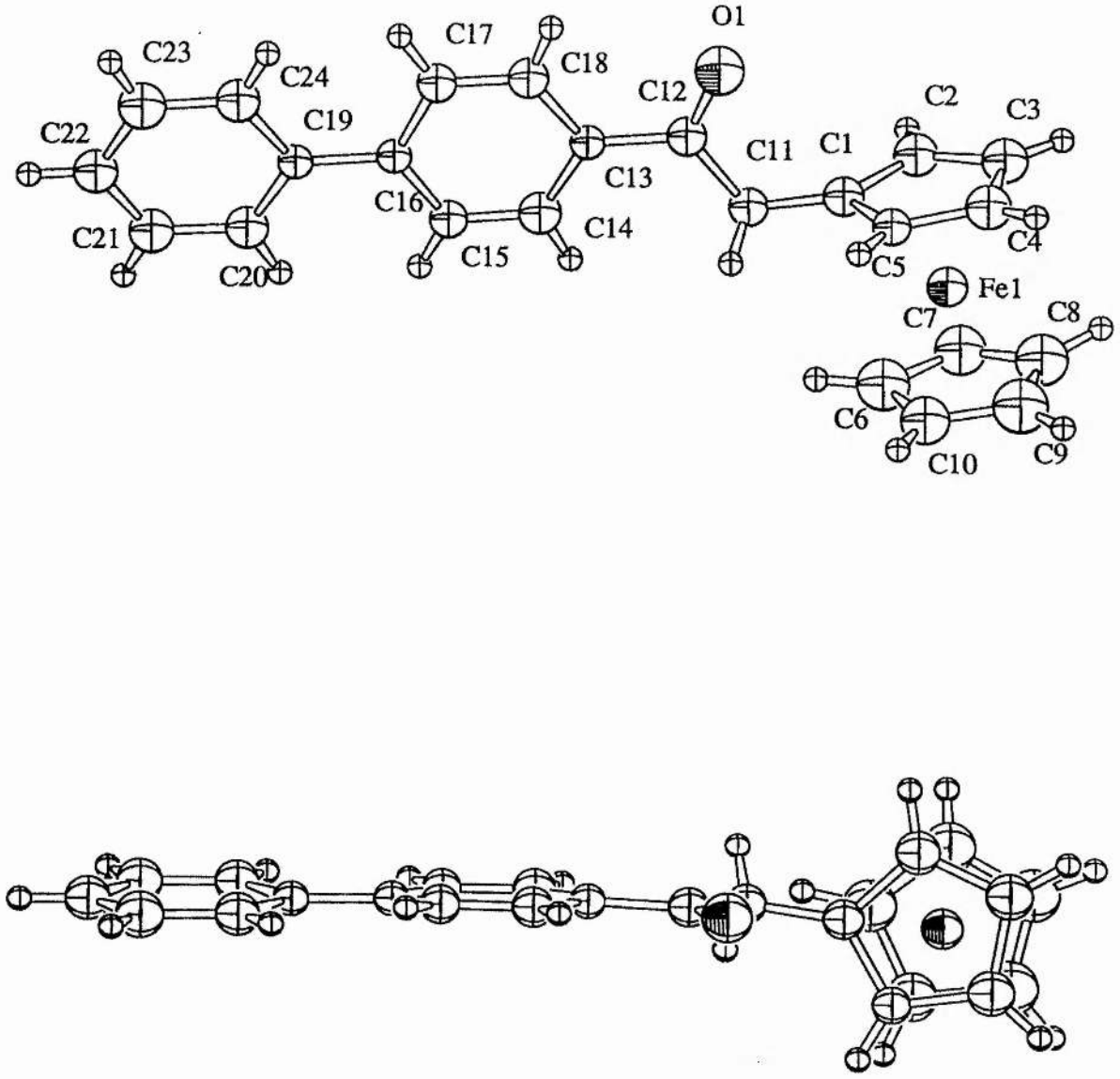


Figure 2.2: Single crystal X-ray structure of 2-ferrocenyl-1-biphenyl-1-ethanone ***39b****, (top) side view of the molecule (bottom) top view of the molecule showing two cp rings almost eclipsed and the two phenyl rings are in the same plane.*
(Adapted from reference 7).

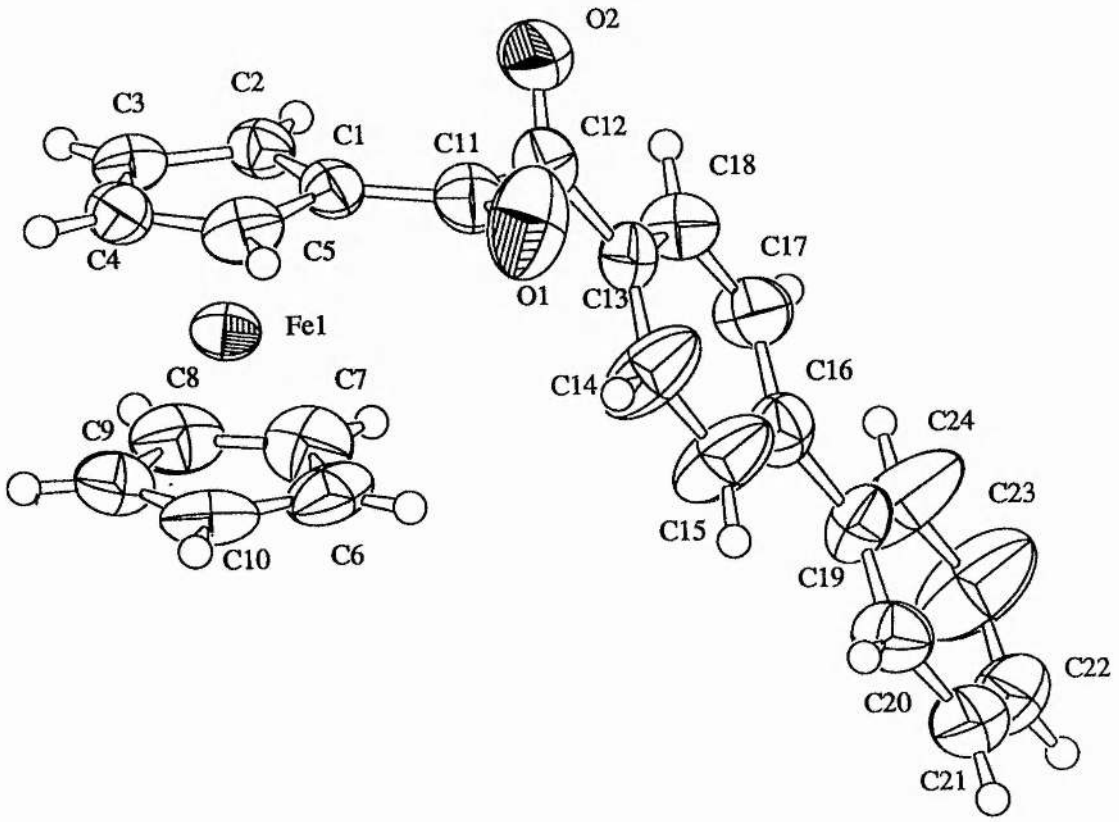


Figure 2.3: Single crystal X-ray structure of ferrocenylbiphenylethanedione ***40b.*** (adapted from reference 6).

2.1.1.5.4 ***Crystal and molecular structures of 42a and 42b.***

The racemic form of compound **42a** crystallizes in the triclinic space group PT with two independent molecules in the asymmetric unit. The structure analysis firstly confirms the constitution of compound **42a** and secondly, indicates that in each of the independent molecules the two stereogenic carbon atoms have the same stereochemistry, so that equal numbers of *RR* and *SS* molecules are accommodated by the centrosymmetric space group.

For a molecule of type $(Cabc)_2$ in which the two stereogenic carbon atoms are of the same hand, then if a, b and c represent mono-atomic substituents, there will be a two-fold rotation axis normal to the central C-C bond, regardless of the conformation adopted by the substituents: only if a, b and c represent poly-atomic substituents with internal conformational degrees of freedom can the molecular symmetry be less than C_2 (Figure 2.4). In both independent molecules of *rac*-**42a** the torsional degrees of freedom, particularly those involving the aryl rings (appendix V) preclude exact C_2 symmetry: however, Figure 2.5 demonstrate clearly the approximate C_2 axes, normal to the C12-C13 and C22-C23 bonds and lying approximately in the plane of the page. Not only is the molecular symmetry only approximately C_2 but, in addition, the four independent -CH(Fc)COPh fragments within the asymmetric unit are all conformationally distinct.

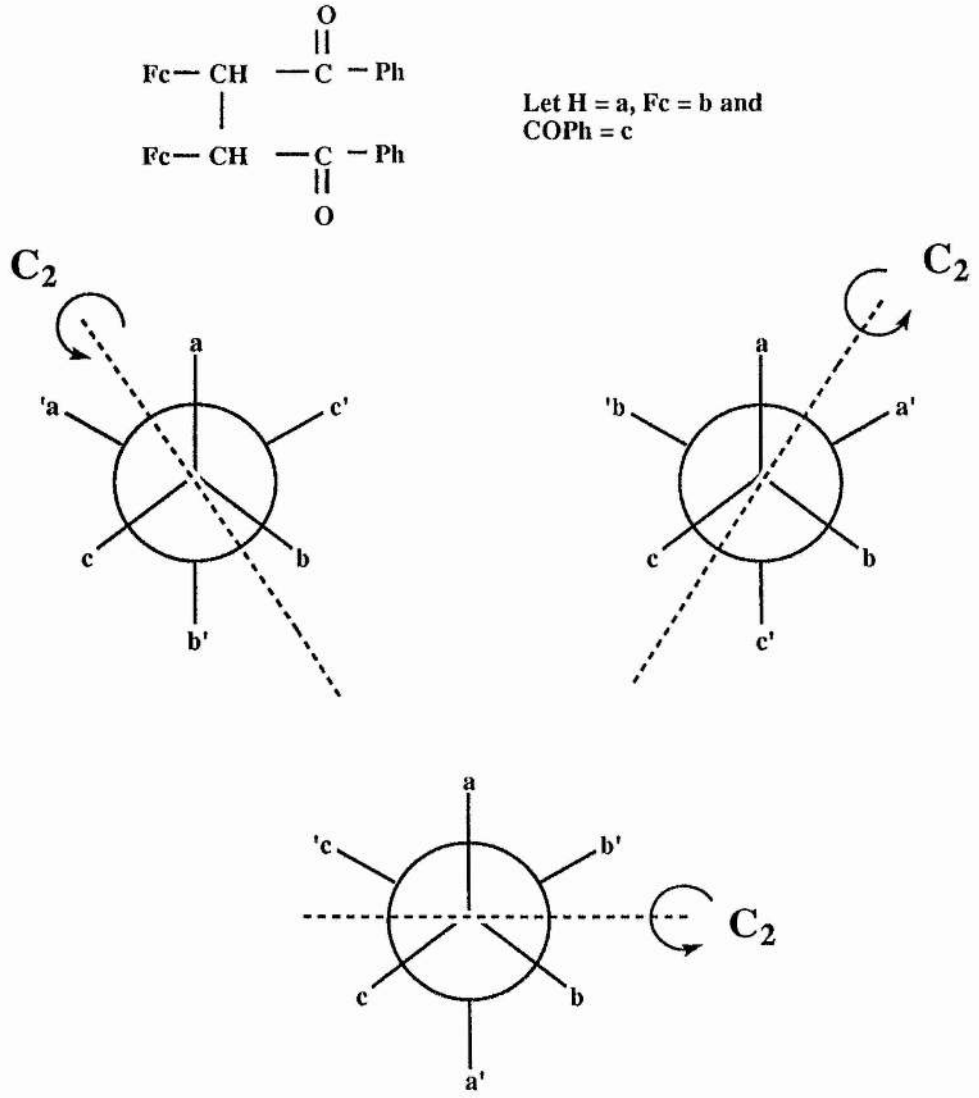


Figure 2.4: A schematic representation that a molecule of type $(Cabc)_2$ has a two fold rotation axis regardless of the positions of the substituents on both the carbons.

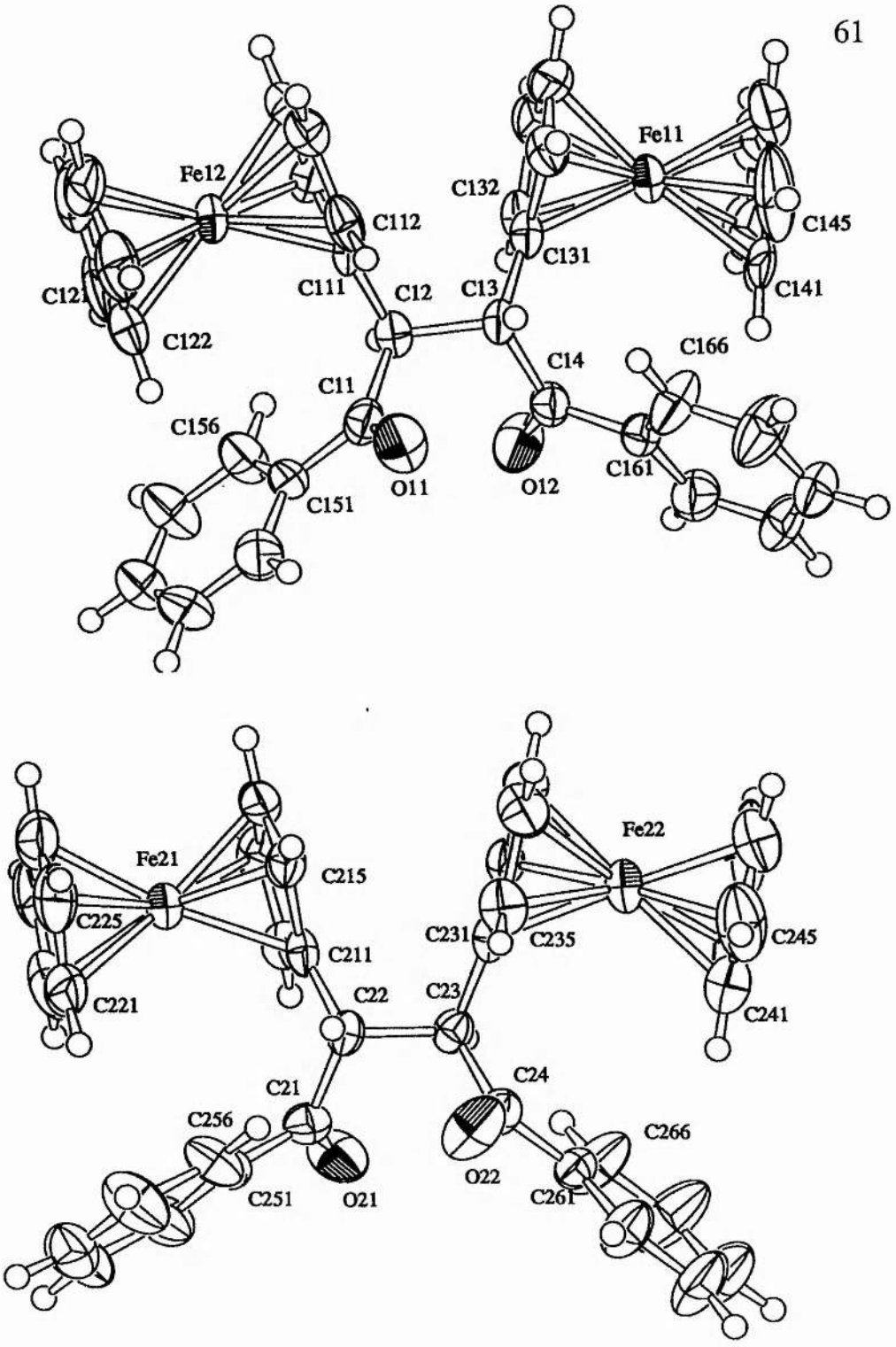


Figure 2.5: Single crystal X-ray structure of racemic 2,3-diferrocenyl-1,4-diphenylbutane-1,4-dione ***42a****; showing both the coupled carbons C12 and C13 (C22 and C23) in RR and SS conformation* (adapted from reference 7).

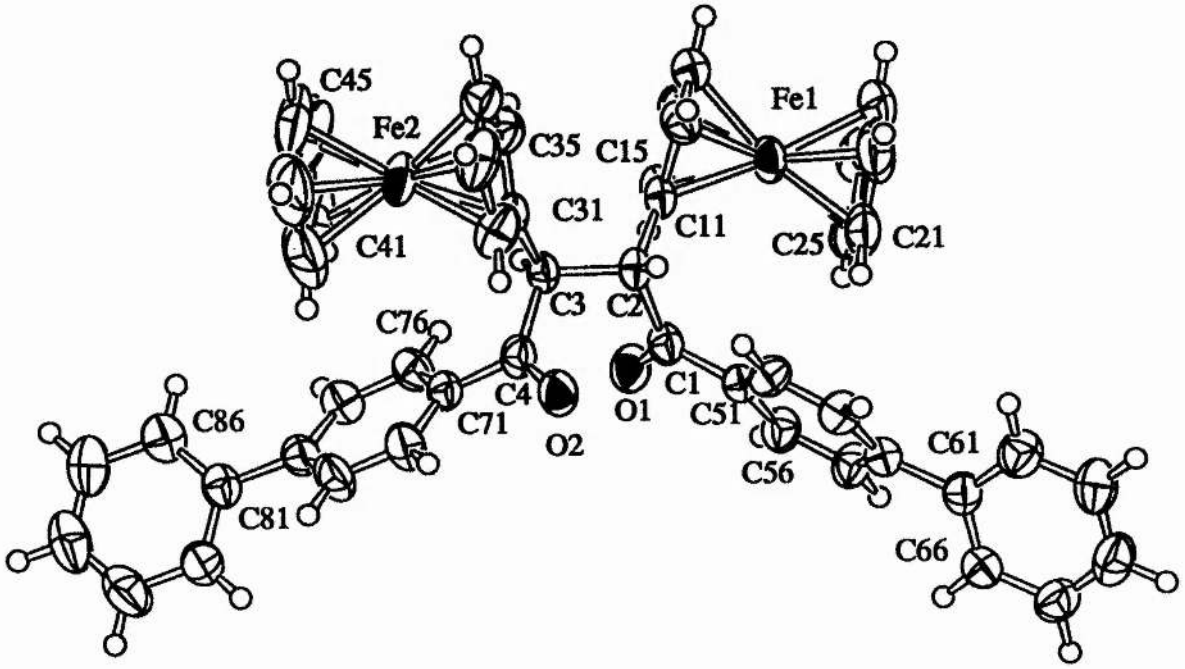


Figure 2.6: Single crystal X-ray structure of racemic 2,3-diferrocenyl-1,4-bis(biphenyl)butane-1,4-dione ***42b.***
(adapted from reference 7)

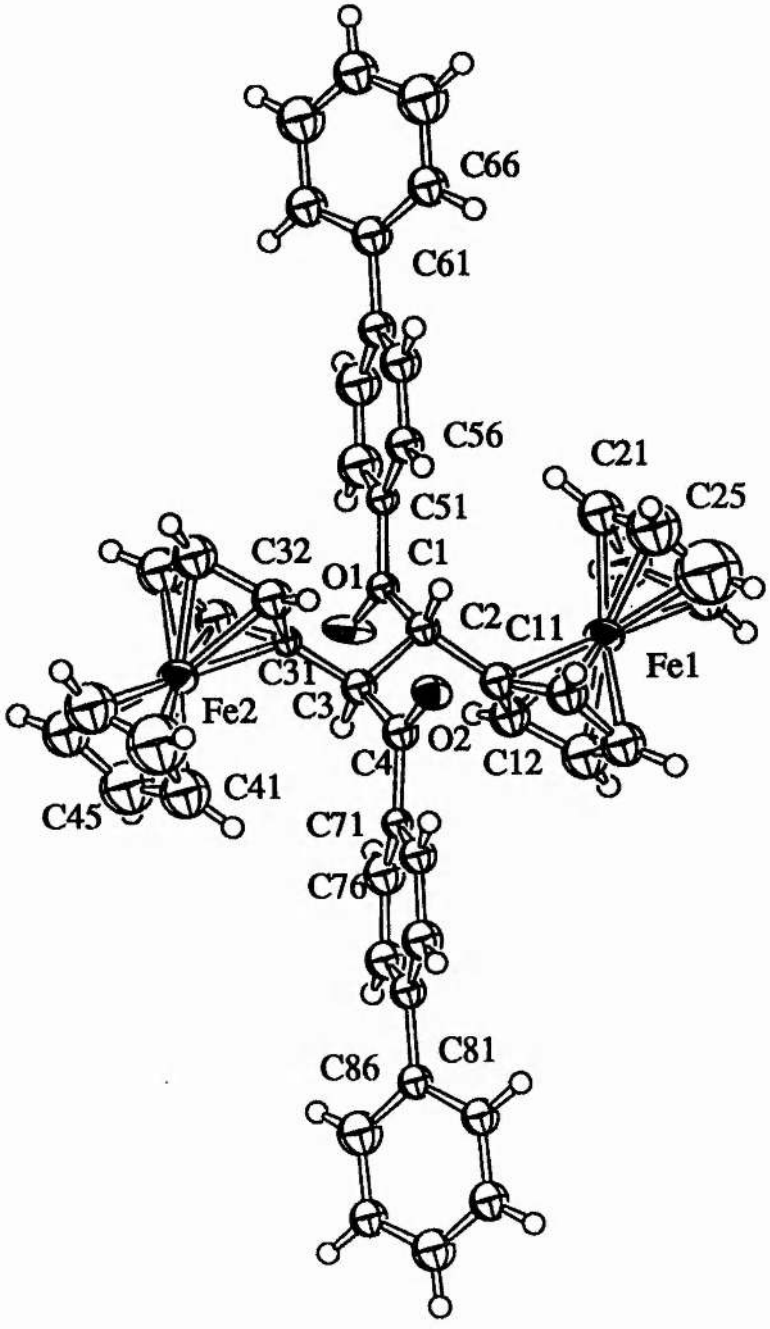


Figure 2.7: Single crystal X-ray structure of meso 2,3-diferrocenyl-1,4-bis(biphenyl)butane-1,4-dione ***42b.***
(adapted from reference 7)

The structures of the two forms of compound **42b** show that these are indeed the *racemic* and *meso* diastereoisomers. *Rac*-**42b** is triclinic, PT, with equal numbers of *RR* and *SS* molecules in the unit cell and, just as found for *rac*-**42a**, the molecules have approximate but not precise two-fold rotational symmetry (Figure 2.6 and crystal data in appendix VI). The *meso* form of **42b** (Figure 2.7) adopts a conformation which is approximately, though not precisely, centrosymmetric, consistent with its *RS* configuration as shown in the schematic representation in Figure 2.8, crystal data are presented in appendix VII. In each of *rac*-**42a**, *rac*-**42b** and *meso*-**42b**, the molecules have the central H-C-C-H fragment in a *trans* conformation; this conformation uniquely minimises the steric repulsions between the four large substituents bonded to the central C_2 fragment. All other staggered conformations require the four large substituents to be adjacent, while if the H-C-C-H is *trans*, only pairwise interactions occur between these large substituents.

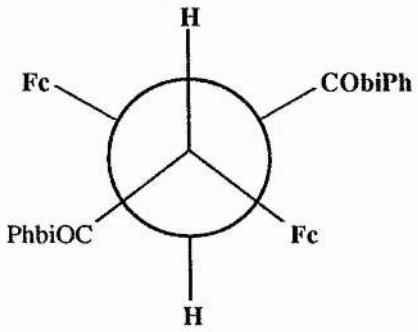
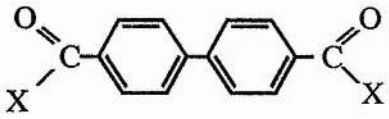


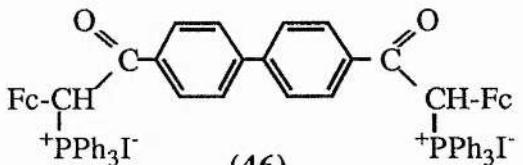
*Figure 2.8: Schematic representation along CH-CH bond in meso-**42b** that shows the molecule is almost centrocemitric.*

2.1.2 Bifunctional 1,2-diketones.

Ferrocene-containing bifunctional diketones were synthesised with a view to further condense with di- or tetra-amines to yield bis- and poly-quinoxalines. Two approaches were investigated for the synthesis of such diketones, in the first approach a bisiodosalt, 4,4'-dicarbonyl-bis[ferrocenylmethyl(triphenylphosphonium iodide)] **46**, like that of **38** under the same reaction conditions, was attempted to synthesise by the reaction of 4,4'-biphenyldicarbonyl chloride **45**, that was synthesised itself by the action of oxalylchloride on 4,4'-biphenyldicarboxylic acid **44** and ferrocenyl phosphorane **37**. The reaction was not successful and a mixture of products were found therein, but none of them was found to be **46**, one component of that was characterised as the starting material **36**, but no attempts were made to properly characterise all the products obtained.



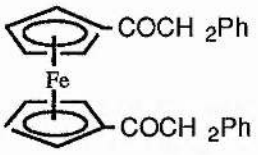
44 X = OH
45 X = Cl



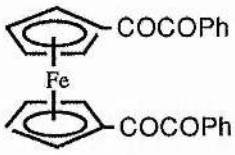
(46)

In the other approach bisacyl ferrocene $Fcd(COCH_2Ph)_2$ **47**, synthesised in one step by Friedel Crafts acylation, was oxidised to ferrocene-1,1'-diylbis(phenylethanedione) **48** by using very active manganese dioxide at 100 °C. The choice of solvent and temperature are very critical in this oxidation; lower temperatures show either no reaction at all or very little oxidation to the required product, or oxidation of the methylene group attached to the one ring only, while at temperatures above 105 °C decomposition is observed. 1,1,2-trichloroethane or

chlorobenzene were found to be the right solvents for this oxidation with a narrow temperature band of 95-105 °C.



(47)



(48)

The course of reaction was followed by TLC; in the first few hours of the reaction two red spots appeared other than the starting material, one of them of higher R_f than the other. The lower R_f value spot, presumably the mono-oxidised intermediate, disappeared slowly by the end of the reaction time and finally only one red spot with no unreacted starting material was observed on TLC with the bisdiketone **48** as the sole product in moderate yield. The compounds **47** and **48** were characterised by NMR and elemental analysis; further condensation of bisdiketone **48** with aromatic di- and tetra-amines to yield quinoxaline compounds is also a proof of its chemical nature (chapter 3).

2.2 EXPERIMENTAL DETAILS

NMR spectra were recorded at ambient temperatures, all ^{13}C spectra were recorded as decoupled, in $CDCl_3$ solution unless stated otherwise, on a Bruker AM-300 spectrometer operating at 300.135 MHz for ^{1}H and 75.469 MHz for ^{13}C. Elemental analysis was carried out in the microanalytical laboratory of the School of Chemistry. Diethyl ether and light petroleum (b.p. 40-60 °C) were dried over sodium wire, and dichloromethane was distilled over calcium hydride prior to use. All the other chemicals were used as received unless stated otherwise.

2.2.1 Synthesis of monofunctional diketones.

The synthesis of monofunctional diketone was carried out by the oxidation of monoketones, which themselves were synthesised as follows.

2.2.1.1 Synthesis of Ferrocenylaryl monoketone.

2.2.1.1.1 Synthesis of *N,N,N',N'*-tetramethyldiaminomethane.

To an ice-cold 1 litre Erlenmayer flask containing 40% aqueous formaldehyde solution (75 cm^3, 1 mol) was added a 40% aqueous dimethylamine solution (225 cm^3, 2 mol) dropwise while stirring. When the addition was complete, the mixture was kept in the ice bath for further 2 h. After this time solid KOH was added to this mixture until two layers had separated. The mixture was warmed to the room temperature and upper organic layer was separated and dried over KOH. The product was distilled after filtration to give *N,N,N',N'*-tetramethyldiaminomethane **33** as a colourless liquid (68.2 g, 70%). b.p. 81-83 °C (lit. 82-83 °C).[1]

δ_H ($CDCl_3$) 1.20 (12H, s, CH_3) and 2.69 (2H, s, CH_2).
δ_C ($CDCl_3$) 42.6 (4C, s, CH_3) and 82.9 (1C, s, CH_2).

2.2.1.1.2 Synthesis of *N,N*-dimethylaminomethylferrocene.

N,N,N',N'-tetramethyldiaminomethane (25.5 g, 250 mmol), solid paraformaldehyde (7.9g, 250 mmol) and glacial acetic acid (200g) were heated on an electrical mantle in a 1 litre three neck flask and were stirred using a mechanical stirrer. When the mixture became homogeneous, ferrocene (93 g, 500 mmol) was added and whole mixture was refluxed

for 5 h. After this time the whole mixture was allowed to cooled to the room temperature and was mixed with water (500 cm^3). The resultant mixture was filtered and the solid residue was washed with dilute acetic acid (50 cm^3). The filtrate was chilled in ice bath and was made alkaline (*ca.* pH 10) by adding solid NaOH pellets; the alkalinity was checked by pH paper. It should be noted that if the solution is not sufficiently alkaline the total recovery of product would not be possible. The product was extracted into diethyl ether (3 x 200 cm^3) and the collected ether extract was washed with water (200 cm^3), dried ($Na_2 SO_4$) and the solvent was removed to give *N,N*-dimethylaminomethylferrocene **34** as a reddish brown oil (51.2 g, 84%) $b.p._{0.45\ mm\ Hg}$ 91-93 °C.

δ_H ($CDCl_3$) 2.10 (6H, s, CH_3), 3.22 (2H, s, CH_2), 3.97 (2H, C_5H_4), 4.05 (5H, s, C_5H_5) and 4.12 (2H, C_5H_4).
δ_C ($CDCl_3$) 43.6 (2C, s, CH_3), 57.9 (1C, s, CH_2), 66.9 (2C, s, C_5H_4), 67.4 (5C, s, C_5H_5), 69.0 (2C, s, C_5H_4) and 82.0 (1C, s, *ipso* C_5H_4)

2.2.1.1.3 Synthesis of (ferrocenylmethyl)trimethylammonium iodide.

To an ice-cold stirred solution of *N,N*-dimethylaminomethyl-ferrocene (50.0 g, 205 mmol) in absolute methanol (100 cm^3) was added dropwise a solution of methyl iodide (45.4 g, 320 mmol) in absolute methanol (50 cm^3) using a dropping funnel. The mixture was then refluxed for 10 min. After cooling the resultant mixture was poured into diethyl ether (500 cm^3) while stirring. (Ferrocenylmethyl)trimethyl-ammonium iodide **35** was precipitated as a yellow crystalline solid (71.4 g, 90%). The solid product was filtered, washed with ether and dried. m.p. 215-219 °C dec. (lit. 215-220 °C).[2]

$\delta_H(CD_3OD)$ 3.05 (9H, s, CH_3), 3.38 (2H, s, CH_2), 4.29 (5H, s, C_5H_5), 4.42 (2H, C_5H_4) and 4.84 (2H, C_5H_4).
$\delta_C(CD_3OD)$ 52.8 (3C, s, CH_3), 68.2 (1C, s, CH_2), 70.4 (5C, s, C_5H_5), 71.7 (2C, s, C_5H_4), 73.4 (2C, s, C_5H_4) and 74.0 (1C, s, *ipso* C_5H_4).

2.2.1.1.4 Synthesis of (ferrocenylmethyl)triphenylphosphonium iodide.

To a solution of (ferrocenylmethyl)trimethylammonium iodide (21.2 g, 55 mmol) in absolute ethanol (600 cm^3) was added triphenylphosphine (26.3 g, 100 mmol). The mixture was refluxed for 24 h. After cooling, the reaction mixture was poured into diethyl ether (800 cm^3) while stirring. (Ferrocenylmethyl)triphenylphosphonium iodide **36** was precipitated as yellow crystals (29.1 g, 90%). The precipitate was filtered, washed with ether and dried m.p. 253-256 °C (lit. 254-256 °C)[4].

$\delta_H(CD_3OD)$ 3.96 (2H, m, C_5H_4), 4.16 (2H, m, C_5H_4), 4.28 (5H, s, C_5H_5), 4.71 [2H, d, CH_2, *J* (HP) 10 Hz] and 7.60-7.90 (15H, m, C_6H_5).
$\delta_C(CD_3OD)$ 27.2 [1C, d, CH_2, *J* (PC) 46 Hz], 70.2 (2C, s, C_5H_4), 70.6 (5C, s, C_5H_5), 71.6 (2C, s, C_5H_4), 75.5 (1C, s, *ipso* C_5H_4), 119.6 [3C, d, *ipso* C_6H_5, *J* (PC) 85 Hz], 131.3 [6C, d, C_6H_5, *J* (PC) 12.4 Hz], 135.4 [6C, d, C_6H_5, *J* (PC) 9.8 Hz] and 136.3 [3C, d, C_6H_5, *J* (PC) 2.4 Hz].

2.2.1.1.5 Synthesis of (ferrocenylmethylene)triphenylphosphorane.

In a 500 cm^3 three neck flask fitted with a bubbler (ferrocenylmethyl)triphenylphosphonium iodide (5.95 g, 10.0 mmol) was suspended in sodium dried diethyl ether (300 cm^3). Oxygen-free nitrogen was passed over the stirred mixture for 5 min. Phenyllithium (1.8 M solution in hexane/ether; 6.4 cm^3, 11.5 mmol) was transferred from Aldrich

'Sureseal' bottle under positive pressure of oxygen-free nitrogen. The reaction mixture was stirred for 3 h under nitrogen atmosphere, and then the synthesis of (ferrocenylmethylene)triphenylphosphorane **37** was complete. A dark red solution was obtained.

2.2.1.1.6 Synthesis of (α-ferrocenylacyl)triphenylphosphonium Iodides.

(Ferrocenylmethylene)triphenylphosphorane was prepared as described above and typically, the acyl chloride 11.5 mmol (benzoyl chloride 1.62 g) was added dropwise (if the acyl chloride was solid as in the case of 4-biphenylcarbonyl chloride it (2.5 g) was added as solution in minimum quantity of dry THF). The colour of the reaction mixture changed from dark red to faint red. The mixture was allowed to stir for further 2 h. The crude solid product was separated by filtration and recrystallized from hot aqueous acetone (25:100 cm^3) mixture. Deep red crystals of compound **38** were filtered off and washed with cold acetone. Yields (α-ferrocenylphenacyl)-triphenylphosphonium iodide **38a** (5.72 g, 82.6%) and (α-ferrocenyl-biphenacyl)triphenylphosphonium iodide **38b** (5.61 g, 73%).

For (α-ferrocenylphenacyl)triphenylphosphonium iodide **38a**:
Anal. found C, 62.1%; H, 4.5%; $C_{36}H_{30}FeIOP$ requires C, 62.4%; H, 4.4%; m.p. 175.5-177.5 °C (lit. 176-179 °C).[4]
$\delta_H(CDCl_3)$ 3.82 (1H, s, C_5H_4), 3.84 (5H, s, C_5H_5), 4.08 (1H, s, C_5H_4), 4.25 (1H, s, C_5H_4), 4.91 (1H, s, C_5H_4), 7.50 (1H, CH), 7.55-8.35 (20H, m, C_6H_5).

$\delta_C(CDCl_3)$ 46.2 [1C, d, CH, *J* (PC) 43.7 Hz], 68.8 (1C, s, C_5H_4), 69.0 (1C, s, C_5H_4), 69.7 (1C, s, C_5H_4), 69.9 (5C, s, C_5H_5), 71.9 (1C, s, C_5H_4), 73.8 (1C, s, *ipso* C_5H_4), 117.5 [3C, d, *ipso* C_6H_5-P, *J* (PC) 83.8 Hz], 129.6 (2C, s, C_6H_5-CO), 129.8 [6C, d, C_6H_5-P, *J* (PC) 12.6 Hz], 130.8 (2C, s, C_6H_5-CO), 134.4 (1C, s, C_6H_5-CO), 134.8 [3C, d, C_6H_5-P, *J* (PC) 2.2 Hz], 135.6 [6C, d, C_6H_5-P, *J* (PC) 9.7 Hz], 136.0 (1C, s, *ipso* C_6H_5-CO), 192.5 (1C, s, CO).

For (α-ferrocenylbiphenacyl)triphenylphosphonium iodide **38b**:
Anal. found C, 65.3%; H, 4.9%; $C_{42}H_{34}FeIOP$ requires C, 65.6%; H, 4.5%; m.p. 161.0-163.0 °C.
$\delta_H(CDCl_3)$ 3.82 (1H, s, C_5H_4), 3.88 (5H, s, C_5H_5), 4.08 (1H, s, C_5H_4), 4.24 (1H, s, C_5H_4), 4.92 (1H, s, C_5H_4), 7.40 (1H, CH), 7.42-7.96 (24H, m, Ph and or biPh).
$\delta_C(CDCl_3)$ 46.2 [1C, d, CH, *J* (PC) 43.6 Hz], 68.7 (1C, s, C_5H_4), 68.8 (1C, s, C_5H_4), 69.6 (1C, s, C_5H_4), 69.8 (5C, s, C_5H_5), 71.9 (1C, s, C_5H_4), 73.8 (1C, s, *ipso* C_5H_4), 117.5 [3C, d, *ipso* C_6H_5-P, *J* (PC) 84.1 Hz], 127.3 (Ph), 127.8 (Ph), 128.5 (Ph), 128.8 (Ph), 129.7 [6C, d, C_6H_5-P, *J* (PC) 12.7 Hz], 131.5 (Ph), 131.9 (1C, s, *ipso* Ph-P), 134.6 (Ph), 135.1 [6C, d, C_6H_5-P, *J* (PC) 9.7 Hz], 139.0 (1C, s, *ipso* biPh), 147.3 (1C, s, *ipso* biPh),191.8 (1C, s, CO).

2.2.1.1.7 Synthesis of 2-ferrocenyl-1-aryl-1-ethanones.

Typically, in a 250 cm^3 three neck flask (α-ferrocenylphenacyl)-triphenylphosphonium iodide (1.5 g, 2.17 mmol) was dissolved in dichloromethane (50 cm^3) and zinc dust (20 g) was added. The mixture was stirred mechanically, and glacial acetic acid (30 cm^3) was added

dropwise while refluxing. When the addition of acetic acid was complete, the mixture was further kept stirred and refluxed for 1 h, and then poured into water (100 cm^3) after cooling to the room temperature. The organic layer was separated and the aqueous phase was also extracted with dichloromethane (3 x 50 cm^3). The combined dichloromethane extracts were washed with water (100 cm^3), dried (Na_2SO_4) and concentrated. Tlc indicated two spots, corresponding to triphenylphosphine and phenacylferrocene. The concentrated mixture was chromatographed on silica gel using dichloromethane as mobile phase to give the phenacylferrocene as a yellow solution. The solvent was removed at ambient temperature to give yellow plate-like crystals, the compound is very sensitive towards atmospheric oxygen. Yields: 2-ferrocenyl-1-phenyl-1-ethanone **39a** (0.46 g, 70%), 2-ferrocenyl-1-biphenyl-1-ethanone **39b** (72.7%). Compound **39a** was too labile for elemental analysis.

For 2-ferrocenyl-1-phenyl-1-ethanone **39a**:
$\delta_H(CDCl_3)$ 3.98 (2H, s, CH_2), 4.12 (5H, s, C_5H_5), 4.15 (2H, s, C_5H_4), 4.20 (2H, s, C_5H_4), 7.48 (2H, t, C_6H_5), 7.58 (1H, d, C_6H_5) and 8.0 (2H, d, C_6H_5).
$\delta_C(CDCl_3)$ 39.4 (1C, s, CH_2), 67.9 (2C, s, C_5H_4), 68.8 (5C, s, C_5H_5), 69.1 (2C, s, C_5H_4), 81.1 (1C, s, *ipso* C_5H_4), 128.6 (2C, s, C_6H_5), 128.6 (2C, s, C_6H_5), 133.1 (1C, s, C_6H_5), 136.8 (1C, s, *ipso* C_6H_5) and 197.3 (1C, s, CO).

For 2-ferrocenyl-1-biphenyl-1-ethanone **39b**:
Anal. found C, 75.5%; H, 5.4%; $C_{24}H_{20}FeO$ requires C, 75.8%; H, 5.3%.
m.p.142.5-144.0 °C.

$\delta_H(CDCl_3)$ 4.02 (2H, s, CH_2), 4.12 (2H, s, C_5H_4), 4.15 (5H, s, C_5H_5), 4.20 (2H, s, C_5H_4), 7.42 (1H, d, C_6H_5), 7.50 (2H, t, C_6H_5), 7.65 (2H, d, C_6H_5 or C_6H_4), 7.71 (2H, d, C_6H_5 or C_6H_4) and 8.08 (2H, d, C_6H_4).
$\delta_C(CDCl_3)$ 39.5 (1C, s, CH_2), 67.9 (2C, s, C_5H_4), 68.8 (5C, s, C_5H_5), 69.1 (2C, s, C_5H_4), 81.2 (1C, s, *ipso* C_5H_4), 127.1 (1C, s, biPh), 127.3 (2C, s, biPh), 128.2 (2C, s, biPh), 129.0 (2C, s, biPh), 129.2 (2C, s, biPh), 135.5 (1C, s, *ipso* biPh), 139.9 (1C, s, *ipso* biPh), 145.8 (1C, s, *ipso* biPh) and 196.9 (1C, s, CO).

2.2.1.1.8 Synthesis of 1-ferrocenyl-2-phenyl-1-ethanone.

To a stirred solution of ferrocene (9.3g, 0.05 mol) in CH_2Cl_2 (50 cm^3) at 0 °C and under N_2 was added in portions a mixture of phenylacetyl chloride (6.67g, 0.05 mol) and $AlCl_3$ (7.72g, 0.05 mol) in CH_2Cl_2 (100 cm^3) over a period of 30 minutes. After 20h, the mixture was poured onto ice, and the whole mixture extracted with CH_2Cl_2 (2 x 50 cm^3); the organic extract was washed with water, dried (Na_2SO_4) and evaporated to give 1-ferrocenyl-2-phenyl-1-ethanone **41** as a reddish brown powder (12.8g, 84.%). m.p. 127.5-129.5 °C (lit. 128-129 °C).[8]
$\delta_H(CDCl_3)$ 3.98 (2H, s, CH_2), 4.08 (5H, s, C_5H_5), 4.48 (2H, s, C_5H_4), 4.80 (2H, s, C_5H_4), 7.30-7.40 (5H, m, C_6H_5).
$\delta_C(CDCl_3)$ 46.8 (1C, s, CH_2), 69.7 (2C, s, C_5H_4), 69.8 (5C, s, C_5H_5), 72.4 (2C, s, C_5H_4), 78.7 (1C, s, *ipso* C_5H_4), 126.8 (1C, s, C_6H_5), 128.5 (2C, s, C_6H_5), 129.3 (2C, s, C_6H_5), 135.2 (1C, s, *ipso* C_6H_5) and 201.8 (1C, s, CO). The use of more than one equivalent of acylating agent lead to the synthesis of bis acyl product also.

2.2.1.2 Oxidation of Ferrocenylmonoketones.

2.2.1.2.1 Oxidation of ferrocenylarylmonoketones by manganese dioxide.

Typically, 2-ferrocenyl-1-phenyl-1-ethanone **39a** (1.4 g, 4.5 mmol) and activated manganese dioxide (8.0. g) were refluxed in dichloromethane (50 cm^3) for four hours. After cooling to room temperature the mixture was filtered and the residue was washed with dichloromethane. Tlc experiment showed two products. Chromatography on silica gel using dichloromethane as eluting solvent yielded 1-ferrocenyl-2-arylethanedione **40** and ferrocenecarboxaldehyde **43.** Typical yields diketone 60-63% ferrocenecarboxaldehyde 32-35%.

For 1-ferrocenyl-2-phenylethanedione **40a**:
Anal. found C, 68.3%; H, 4.9%; $C_{18}H_{14}FeO_2$ requires C, 68.0%; H, 4.4%. m.p. 84-86 °C (lit. 85-86 °C).[8]
$\delta_H(CDCl_3)$ 4.30 (5H, s, C_5H_4), 4.70 (2H, t, C_5H_4), 4.90 (2H, t, C_5H_4), 7.50 (2H, t, C_6H_5), 7.62 (1H, d, C_6H_5) and 8.05 (2H, d, C_6H_5).
$\delta_C(CDCl_3)$ 70.51 (2C, s, C_5H_4), 70.59 (5C, s, C_5H_5), 73.92 (2C, s, C_5H_4), 74.55 (1C, s, *ipso* C_5H_4), 128.83 (2C, s, C_6H_5), 129.93 (2C, s, C_6H_5), 133.02 (1C, s, *ipso* C_6H_5), 134.42 (1C, s, C_6H_5), 192.82 (1C, s, CO) and 198.99 (1C, s, CO).

For 1-Ferrocenyl-2-biphenylethanedione **40b**:
Anal. found C, 72.9%; H, 4.8%; $C_{22}H_{18}FeO_2$ requires C, 73.1%; H, 4.6%; m.p. 120.5-122.0 °C.

$\delta_H(CDCl_3)$ 4.30 (5H, s, C_5H_5), 4.72 (2H, s, C_5H_4), 4.92 (2H, s, C_5H_4), 7.45 (1H, d, C_6H_5), 7.52 (2H, t, C_6H_5), 7.67 (2H, d, C_6H_5 or C_6H_4), 7.78 (2H, d, C_6H_5 or C_6H_4) and 8.15 (2H, d, C_6H_4).
$\delta_C(CDCl_3)$ 70.6 (5C, s, C_5H_5), 70.6 (2C, s, C_5H_4), 73.9 (2C, s, C_5H_4), 74.6 (1C, s, *ipso* C_5H_4), 127.4 (2C, s, biPh), 127.5 (2C, s, biPh), 128.5 (1C, s, biPh), 129.0 (2C, s, biPh), 130.5 (2C, s, biPh), 131.7 (1C, s, *ipso* biPh), 139.7 (1C, s, *ipso* biPh), 147.1 (1C, s, *ipso* biPh), 192.4 (1C, s, CO) and 198.9 (1C, s, CO).

For ferrocenecarboxaldehyde **43**:
$\delta_H(CDCl_3)$ 4.30 (5H, s, C_5H_5), 4.60 (2H, C_5H_4), 4.80 (2H, C_5H_4) and 9.95 (1H, s, CHO).
$\delta_C(CDCl_3)$ 69.7 (5C, s, C_5H_5), 73.3(4C, s, C_5H_4), 79.5 (1C, s, *ipso*-C_5H_4) and 193.6 (1C, s, CHO); m.p. 119-120 °C (lit. 119-120 °C).[12]

2.2.1.2.2 Oxidation of ferrocenylarylmonoketones by selenium dioxide.

Typically, the monoketone **39** (2.36 mmol) was added to a suspension of powdered selenium dioxide (0.9g, 8.1 mmol) in acetic anhydride (10 cm^3). This mixture was heated under reflux, and its composition was monitored by TLC; when the starting material **39** was all consumed (typically ca 4 h), the mixture was cooled to ambient temperature and filtered, and the residue was washed with more acetic anhydride (5 cm^3). The combined filtrate and washings were hydrolysed with water (20 cm^3) and this solution was neutralised with sodium hydrogencarbonate. The neutral aqueous solution was extracted with dichloromethane (3 x 50 cm^3); this extract was washed with water (100

cm^3) and dried ($MgSO_4$), and the solvent was removed. Chromatography on silica with dichloromethane as eluent yielded yellow **42a** or **42b** (typical yields 55-70%) as mixtures of diastereoisomers (NMR), followed by red **40a** or **40b** (typical yields 10-15%). Further chromatography of the yellow components on silica using CH_2Cl_2/light petroleum (3:1 v/v) yielded for **42a**, firstly the pure racemic product, followed by a mixture of diastereoisomers, and for **42b** each diastereoisomer in pure form, accompanied by a mixed fraction.

Safety Note: The unreacted selenium dioxide and all organoselenium residues were first treated with sodium sulfite and then was stored in a separate bottle for special disposal.

Anal. **42a** (*rac/meso* mixture) Found: C 71.0%, H 5.0%; $C_{36}H_{30}Fe_2O_2$ C 71.3%, H 5.0%: **42b** (*rac/meso* mixture) Found: C 76.0%, H 5.1%; $C_{48}H_{38}Fe_2O_2$ requires C 76.0%, H 5.0%.

NMR *rac*-**42a**, δ(H) 3.42 (s, 1H), 3.95 (s, 1H), 4.12 (s, 1H) and 4.17 (s, 1H) (C_5H_4); 3.60 (s, 5H, C_5H_5); 4.78 (s, 1H, CH); 7.5-7.6 (m, 3H) and (8.1-8.2 (m, 2H) (C_6H_5): δ(C) 51.9 (d, CH); 66.2 (d), 67.1 (d), 68.1 (d), 70.5 (d) and 82.1 (s) (C_5H_4); 68.3 (d, C_5H_5); 128.6 (d), 128.7 (d), 133.0 (d) and 138.0(s) (C_6H_5); 199.6 (s, CO): *rac*-**42b**, δ(C) 51.9 (d, CH); 66.9 (d), 67.8 (d), 68.7 (d), 71.0 (d) and 83.0 (s) (C_5H_4); 68.9 (d, C_5H_5); 126.9 (d), 127.2 (d), 128.0 (d), 128.8 (d), 130.0 (d), 136.7 (s), 140.0 (s) and 145.4 (s) (C_6H_5); 199.1 (s, CO): *meso*-**42b**, δ(C) 51.9 (d, CH); 66.8 (d), 67.7 (d), 68.6 (d), 70.9 (d) and 83.0 (s) (C_5H_4); 68.8 (d, C_5H_5); 127.2 (d), 127.3 (d), 128.5 (d), 129.2 (d), 129.4 (d), 136.7 (s), 149.8 (s) and 145.7 (s) (C_6H_5); 199.1 (s, CO).

2.2.1.2.3. Oxidation of (α-ferrocenylphenacyl)triphenylphosphonium iodide by selenium dioxide.

The (α-ferrocenylphenacyl)triphenylphosphonium iodide **38a** (4.0 g, 5.78 mmol) was added to a suspension of selenium dioxide (7.0 g, 63 mmol) in 20% aqueous acetone (50 cm^3). The mixture was heated under reflux for 2h, cooled, and filtered; the solid residue was washed with dichloromethane (2 x 50 cm^3). Sufficient water and dichloromethane were added to the combined filtrate and washings until two layers separated. The organic layer was dried and the solvents removed. Chromatography on silica gel yielded red 2-ferrocenyl-1-phenylethanedione **40a** (1.1 g, 3.46 mmol, 60%). Confirmed by ^1H and ^{13}C NMR.

Safety Note: The unreacted selenium dioxide and all organoselenium residues were first treated with sodium sulfite and then was stored in a separate bottle for special disposal.

2.2.1.2.4 Oxidation of acyl ferrocene by manganese dioxide.

Acyl ferrocene, 1-ferrocenyl-2-phenyl-1-ethanone (1.0 g, 3.3 mmol) **41** and very active manganese dioxide (2.4 g, 27.5 mmol) were heated under reflux in 1,1,2-trichloroethane (50 cm^3) for 24 h. TLC of the crude reaction mixture showed the red spot for diketone. The mixture was cooled and filtered, the residue was washed with dichloromethane and the combined filtrate was concentrated under reduced pressure. Purification by silica gel column using dichloromethane as mobile phase followed by crystallisation afforded diketone **40a** as red solid. Characterised by ^1H and ^{13}C NMR.

2.2.2 Synthesis of difunctional ferrocenyldiketones.

2.2.2.1 Synthesis of 4,4'-biphenyl dicarbonyl chloride.

4,4'-biphenyldicarboxylic acid **44** (5.5g, 22.5 mmol), phase transfer catalyst; benzyltriethylammonium chloride (0.03g) and toluene (200 cm^3) were taken in a 500 cm^3 round bottom flask, fitted with reflux condenser were heated over a heating mantle. Oxalyl chloride (5.0 cm^3, 55 mmol) was added using a syringe through a septum. 4,4'-Biphenyldicarboxylic acid is not soluble in toluene but as the reaction proceeds, the acid is converted to the acid chloride which is soluble in the refluxing toluene. After 8 h reflux the solution became clear and the reaction was assumed to be complete. After filtering off the traces of solid residue and boiling chips, the filtrate was evaporated to give pure 4,4'-biphenyl dicarbonyl chloride **45** (6.2 g, 88%), m.p. 183-184.5 °C (lit. 184 °C).[13]

$\delta_H(CDCl_3)$ 7.78 (4H, d, C_6H_4), 8.50 (4H, d, C_6H_4).
$\delta_C(CDCl_3)$ 127.9 (4C, s, C_6H_4), 132.1 (4C, s, C_6H_4), 133.2 (2C, s, *ipso*-C_6H_4-C_6H_4), 145.8 (2C, s, *ipso*-C_6H_4-C_6H_4), 167.9 (2C, s, COCl).

2.2.2.2 Attempted synthesis of 4,4'-dicarconylbis-[ferrocenylmethyl(triphenylphosphonium iodide)].

(Ferrocenylmethylene)triphenylphosphorane was prepared as described in section 2.2.1.1.5 and 4,4'-biphenyl dicarbonyl chloride **45** (5.75 mmol 1.6 g) was added dropwise as a solution in minimum quantity of dry THF. The colour of the reaction mixture changed from dark red to brown. The mixture was allowed to stir for further 2h. The crude solid product was separated by filtration and attempts to crystallize any thing

from hot aqueous acetone as in **38** were unsuccessful. A fraction of the solid residue was not soluble in hot aqueous acetone other soluble part resulted as oil. NMR of both the parts did not showed any expected resonances. Some of the peaks were same as the starting material **36**.

2.2.2.3 Synthesis of 1,1'-bis(phenylacetyl) ferrocene.

A solution of ferrocene **3** (7.0 g, 0.0376 mol) in dichloromethane (100 cm^3) was added dropwise over 35 min, at room temperature and under nitrogen, to a stirred solution of phenylacetyl chloride (11.6 g, 0.0752 mol) and anhydrous $AlCl_3$ (10.0 g, 0.0752 mol) in dichloromethane (400 cm^3). After 24h, the mixture was poured onto ice, and the whole mixture extracted with dichloromethane (2x50 cm^3); the organic extract was washed with water, dried (Na_2SO_4) and evaporated to give a dark red powder. Chromatography on alumina eluting with light petroleum/CH_2Cl_2 yielded 9.9 g (62%) of 1,1'-bis(phenylacetyl) ferrocene **47**. m.p. 148-149 °C. Anal. Found: C, 74.2%; H, 5.2%; $C_{26}H_{22}FeO$ requires C, 74.0%; H, 5.2%.

$\delta_{(H)}$ 3.90 (s, 4H, CH_2), [4.32(m, 4H) and 4.70(m, 4H) (C_5H_4)], 7.25-7.40 (m, 10H, Ph);

$\delta_{(C)}$ 47.0 (s, CH_2), [71.1(s) 73.8(s) and 79.8(s) (C_5H_4)], [126.9(s) 128.6(s) 129.4(s) and 134.8(s) (Ph)], 201.1(s, CO). The use of more than two equivalents of acylating agent led to further acylation of the product.

2.2.2.4 Oxidation of 1,1'-bis(phenylacetyl) ferrocene.

Very active manganese dioxide (14.4g, 165 mmol) was added to a solution of 1,1-bis(phenylacetyl)ferrocene **47** (3.15g, 7.5 mmol) in 1,1,2-trichloroethane (125 cm^3). The mixture was stirred vigorously, and

heated to 100 °C for 24h. After cooling, the mixture was filtered and the solid residue washed with CH_2Cl_2 until the washings were colourless. The combined filtrate and washings were evaporated to give a red-black solid, purification by silica gel column and crystallisation from CH_2Cl_2-light petroleum (1:1 v/v) afforded ferrocene-1,1'-diylbis-(phenylethanedione) **48** in 40% yield. Anal. Found: C, 69.4%; H, 4.2%. $C_{26}H_{18}FeO_4$ requires; C 69.4%; H 4.0%.

$\delta_H(CDCl_3)$ [4.77(s, 4H) and 4.96(s, 4H) (C_5H_4)], 7.4-8.0(m, 10H, Ph); $\delta_C(CDCl_3)$ [72.3(s), 75.6(s, ipso) and 76.1(s) (C_5H_4)], [128.9(s), 130.0(s), 132.5(s, ipso) and 134.7(s) (C_6H_5)], [192.1(s) and 197.8(s) (CO)].

2.2.3 Synthesis of Very Active manganese dioxide.[9]

A very active manganese dioxide was synthesised[7] by adding dropwise a solution of manganese(II) chloride tetrahydrate (22.0 g, 0.11 mol) in water (200 cm^3) at 70 °C, with stirring, to a solution of potassium permanganate (16.0 g, 0.10 mol) in water (200 cm^3) at 70 °C contained in a 2 l. conical flask in a fume hood. A vigorous reaction with evolution of chlorine took place and manganese dioxide precipitated out. The suspension was further stirred for 2 h and was kept overnight at room temperature. The precipitate was filtered off, washed with water (500 cm^3) until the washings showed negligible chloride content ($AgNO_3$), and then dried in the oven at 120 °C for 24 h. Manganese dioxide was obtained as a chocolate brown amorphous powder (18.3 g, 99.8%).

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CHAPTER 3

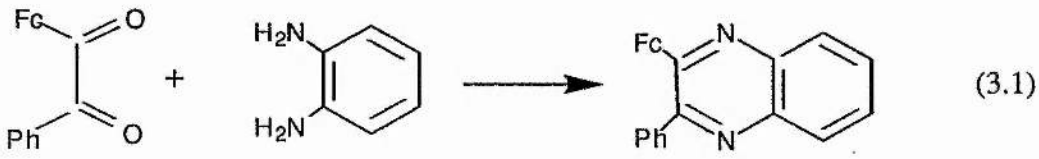
FERROCENE-CONTAINING QUINOXALINES

In this chapter the condensation of ferrocenyl diketones, FcCOCOR, with a variety of aromatic diamines to produce ferrocenyl quinoxalines is described. Electrochemical behaviour of the synthesised ferrocenyl quinoxalines is also studied. Condensation of ferrocenyl diketones, FcCOCOR, and ferrocenediyl bisdiketones, Fc$_2$(COCOR)$_2$, with aromatic tetra- and di-amines respectively, yielded ferrocene-containing bis-quinoxalines. Polycondensation of bisdiketone and aromatic tetra-amine furnished the expected polymeric ferrocene-containing quinoxaline.

3.1 RESULTS AND DISCUSSION

3.1.1 Ferrocene-containing monoquinoxalines.

Quinoxalines can be readily synthesised by the cyclocondensation of 1,2-diketones or alternatively α-halocarbonyl compounds with aromatic 1,2-diamines as described earlier (Equation 1.5 and Equation 1.6). 2-Ferrocenyl-3-phenylquinoxaline **7** was synthesised by the cyclo-condensation of ferrocenyl-1,2-diketone **40a** and 1,2-diaminobenzene **49** (Equation 3.1) in a melt as well as in a solution phase that was further heated to dryness; the yield in the latter case was found to be superior. The products from both the methods were compared and found identical by TLC and ^{1}H and ^{13}C NMR spectroscopy, the m.p. is also consistent with the literature value. The ^{1}H NMR spectrum contains, as well as characteristic signals from the monosubstituted ferrocenyl fragment, well-separated resonances arising from the phenyl and quinoxalyl fragments: the ^{13}C spectrum again shows the characteristic resonances from the ferrocenyl fragment, together with seven CH and five quaternary resonances in the aromatic region. The crystal structure of 2-ferrocenylquinoxaline **6**, synthesised by the reaction of $FcCOCH_2Cl$ and 1,2-diaminobenzene,[1] and 2-ferrocenyl-3-phenylquinoxaline **7**, synthesised in a melt from FcCOCOPh and 1,2-diaminobenzene,[2] have already been reported by Ferguson, Glidewell and Scott.



40a **49** **7** (3.1)

The ferrocenylmonoquinoxalines were synthesised as the first step towards ferrocenylpolyquinoxaline synthesis. These monomeric ferrocenylquinoxalines are themselves of potential interest and importance as a number of quinoxalines are powerful antibiotics and some examples show their potential as anti-cancer drugs;[3] their action in this respect is dependent on their binding to DNA by intercalation.[4] At the same time, some rather simple ferricinium salts have been shown to exhibit powerful anti-tumour activity against a range of human tumour types:[5] the introduction of ferrocenyl substituents onto the quinoxaline framework could perhaps provide, in a single molecular species, a powerful combination of these two actions.

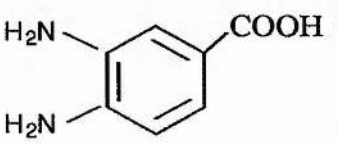
Some substituted ferrocenylphenylquinoxalines have been synthesised by cyclocondensation of substituted aromatic diamines with ferrocenylphenyl 1,2-diketone **40a**; when the diamine is unsymmetrically substituted the quinoxaline formed was a mixture of two regio-isomers, which in some cases were separable by careful chromatography. The yield in the solution form was found higher (65%) than the melt (40-45%) for the parent ferrocenylphenylquinoxaline **7**; therefore all the further reactions were carried out in solution, where the choice of solvent is governed by the solubility of the reactants and its volatility. Nearly all the resulting quinoxalines isolated after chromatography were characterised as hydrates by elemental analysis; either monohydrates or hemi-hydrates. Despite repeated attempts to obtain suitable crystals for single-crystal X-ray analysis of the resulting quinoxalines, no such attempt was successful, presumably because of the presence of more than one regioisomer in the crystallizing solution. However, in the case of

bisquinoxaline **61** (section 3.1.2) suitable crystals were obtained from diethylether/dichloromethane solution and the single-crystal X-ray analysis revealed the presence of a dichloromethane molecule hydrogen bonded to one of the nitrogens of the quinoxaline moiety. This supports the above claim of the presence of water molecule in most of the prepared quinoxalines, because water is a much stronger hydrogen-bond donor than dichloromethane.

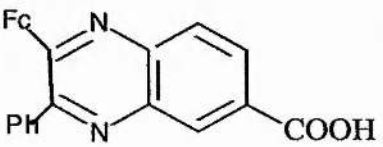
3.1.1.1 Reaction of 40a with 3,4-diaminobenzoic acid.

When 3,4-diaminobenzoic acid **50** was reacted with 1,2-diketone **40a** the resulting quinoxaline **51** was obtained. TLC and both ^{1}H and ^{13}C NMR spectroscopy indicated the presence of the two expected regio-isomers of the substituted quinoxaline, namely 2-ferrocenyl-3-phenyl-quinoxalyl-6-carboxylic acid **51a** and 3-ferrocenyl-2-phenylquinoxalyl-6-carboxylic acid **51b** arising from the alternative orientation of the reactants in the condensation process. The elemental analysis after two crystallizations was not that required theoretically for the pure compound, but both the ^{1}H and ^{13}C NMR spectra were clean. The only assumption that can be made is that perhaps the compound crystallizes as hydrate, and the elemental analysis when compared with the theoretical calculation for mono-hydrate compound seems to be acceptable. Attempts to obtain good crystals suitable for single-crystal X-ray crystallography were unsuccessful because of the presence of both the regio-isomers in the crystallizing solution; these were not found separable under any attempted chromatographic conditions. However, it was possible, despite some peak overlap, to assign the peaks in both ^{1}H and ^{13}C NMR spectrum completely. The ^{1}H NMR spectrum in the ferrocene

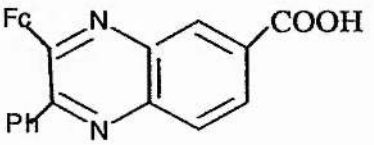
region contains patterns characteristic of the monosubstituted ferrocene, i.e. the peak intensities are 5:2:2 corresponding to unsubstituted and substituted Cp rings respectively. As both the isomers **51a** and **51b** are present in the solution so this pattern is repeated with a relative ratio of 1:2, indicating the relative ratio of the two isomers. The ^{13}C spectrum also indicates the presence of both isomers, except that both the carbonyl carbons appear at the same position and two phenyl/quinoxalyl quaternary carbons are superimposed with some other peaks in the aromatic region. The observation of 22 out of 24 aromatic carbons required resolution enhancement. However in the ferrocene region the eight peaks for the two isomers are very clear.



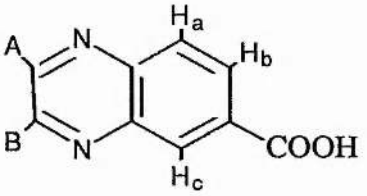
50



51a



51b



A and B are Fc or Ph

51

The ^1H spectrum of the compound **51** is very interesting; three protons on the quinoxaline ring marked H_a, H_b and H_c above appears in the region of 8.15, 8.3 to 8.4 and 8.9 ppm respectively; protons H_a and H_b represent non-first order type AB system. Theoretically a non-first order type system is observed if $\Delta\nu$ is less than $6J$ where ν and J are the peak position and coupling constant (in Hz) respectively[6]. As a result the peaks in the two doublets obtained for H_a and H_b are not equal, but rather

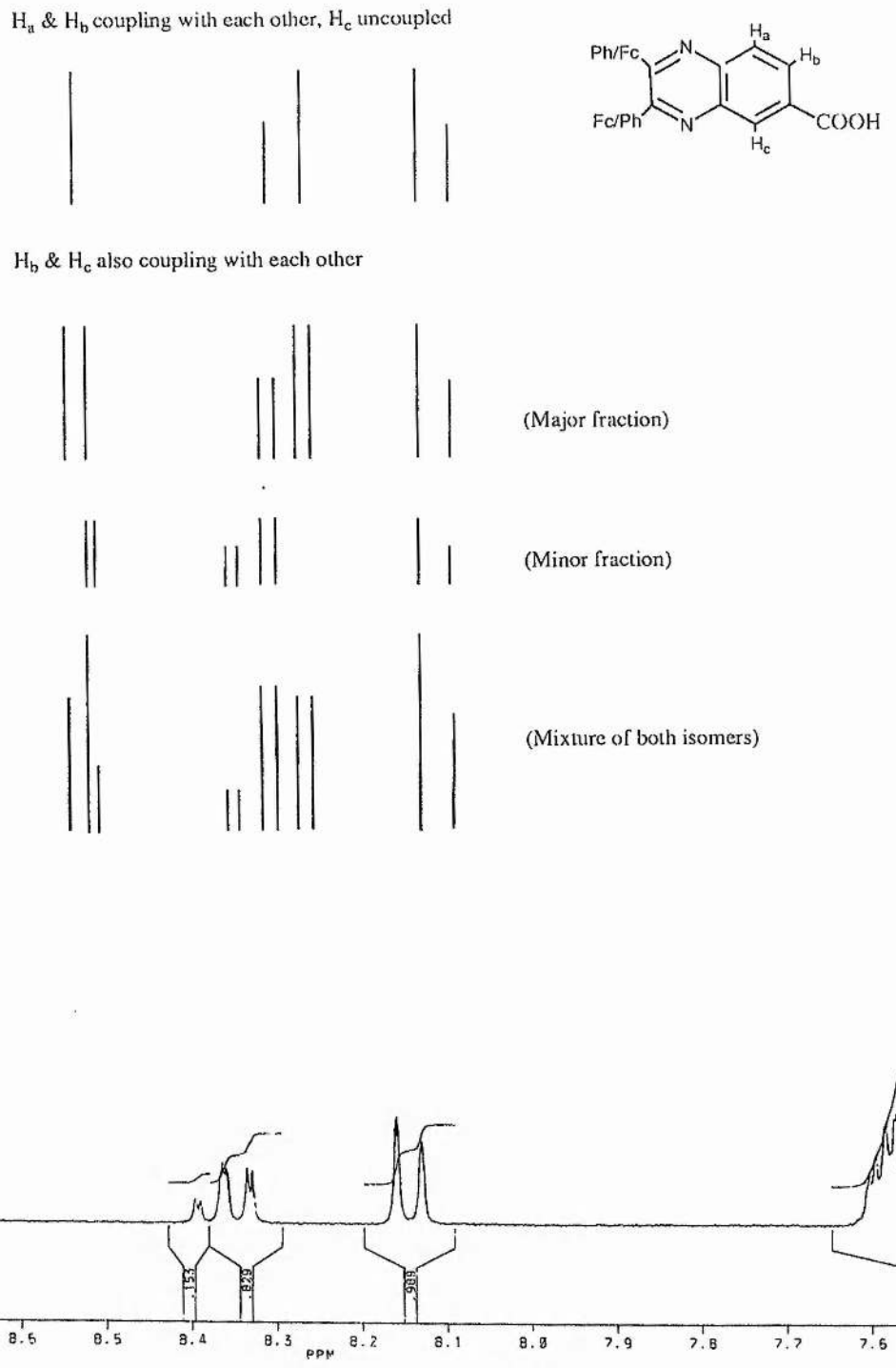


*Figure 3.1: ^1H splitting pattern of H_a, H_b and H_c in **51** (running at 300.135 MHz); below, original spectra; above, schematic representation of splitting pattern.*

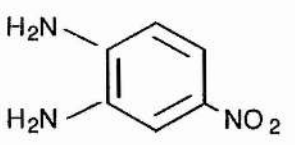
the two central peaks are of higher intensity than the two outer ones. Moreover, H_b and H_c are also coupled to each other via long-range ^4J aromatic coupling, making this an ABX system, in which H_b is being coupled to H_a as well as to H_c by long range coupling through the ring. The presence of two regio isomers, one as major other as minor, makes it even more interesting.

So in the region of the ^1H spectrum between 8.1 and 8.9 ppm, there should be 8 peaks for the major isomer; a doublet for H_a, a doublet of doublets for H_b and again a doublet for H_c, and 8 peaks of almost half the intensity for the minor isomer. The peaks for $H_{a,maj}$ and $H_{a,min}$ appear at the same position, two peaks of $H_{b,maj}$ and $H_{b,min}$ overlap each other and one in $H_{c,maj}$ and $H_{c,min}$ superimpose on each other resulting a doublet for $H_{a,maj,min}$, a triplet for $H_{b,maj,min}$ and an apparent triplet for $H_{c,maj,min}$ (Figure 3.1).

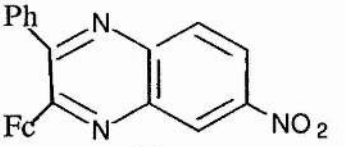
3.1.1.2 Reaction of 40a with 4-Nitro-1,2-diaminobenzene.

The condensation of 4-nitro-1,2-diaminobenzene **52** with 1,2-diketone **40a**, yielded two regio-isomers of the substituted quinoxaline **53**, as expected, namely, 3-ferrocenyl-2-phenyl-6-nitroquinoxaline **53a** and 2-ferrocenyl-3-phenyl-6-nitroquinoxaline **53b**. The peaks in the ^1H NMR spectrum were readily assigned to ferrocenyl and phenyl or quinoxalyl groups. The pattern of the proton NMR spectrum of the mixture of the two isomers of this compound **53** is very much similar to the above compound **51**, because both of them have their substituents at the same positions on the quinoxaline ring and both -COOH and $-NO_2$ groups are ring deactivating, with some variations in the peak overlap.

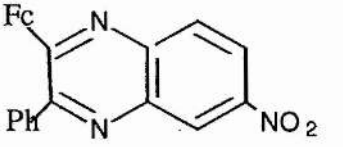
The relative ratio of the two isomers major:minor, calculated from ^{1}H integration in the ferrocene region was found 3:1. The ^{13}C NMR spectrum is also very clear and shows all the representative peaks for ferrocenyl and phenyl or quinoxalyl moieties except one quaternary aromatic carbon peak that presumably appears at the same position as another peak, most probably at 138.9 ppm as the intensity of this peak appears to be doubled, this is also revealed by the comparison of the ^{13}C spectra of a pure fraction of the more abundant isomer and the mixture of both the isomers. Elemental analysis of the mixture of isomers supports the hemihydrate constitution. ^{1}H and ^{13}C NMR and elemental analysis provides sufficient proof for the identity of the compound. The two isomers were inseparable on a silica gel column; an attempt to separate on a neutral alumina column, yielded the less polar, more abundant, isomer pure, enough to carry out NMR spectroscopy along with the mixture of the two isomers. The eluent that appeared to contain a single isomer (by TLC and NMR) was allowed to crystallize slowly from ethyl acetate solution, and single-crystal X-ray crystallography was carried out on the crystals obtained. The structure obtained proved to be in fact a 5:1 mixture of the two isomers with 3-ferrocenyl-2-phenyl-6-nitroquinoxaline **53a** as the major constituent. A discussion of the molecular structure of **53** is given in section 3.1.1.6.



52



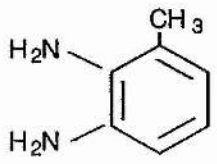
53a



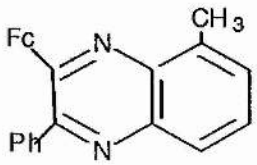
53b

3.1.1.3 Reaction of 40a with 2,3-diaminotoluene.

Another substituted quinoxaline was synthesised by the cyclocondensation of 2,3-diaminotoluene **54** with ferrocenylphenyl-1,2-diketone **40a**. TLC of the crude product shows the presence of the two regio-isomers and these isomers were found to be separable by column chromatography. Both the isomers show a peak in the ^1H NMR spectrum for methyl protons along with the characteristic pattern of monosubstituted ferrocene (5:2:2), the aromatic region showed a multiplet corresponding in intensity to seven protons and a doublet weighing for one proton. The two isomers, 3-ferrocenyl-2-phenyl-5-methylquinoxaline **55a** and 2-ferrocenyl-3-phenyl-5-methylquinoxaline **55b** were judged in the relative ratio of 3:2 from the integration of the methyl protons in ^1H spectrum. The ^{13}C spectrum shows three peaks including one quaternary in the ferrocene region, as one of the peaks represents 2 x CH_2 groups of the substituted Cp ring happens to be superimposed on the single peak of unsubstituted Cp ring of the ferrocenyl moiety. In the aromatic region both the isomers have six quaternary carbons and six non-quaternary carbons of which two peaks represent two carbons and four peaks present one carbon respectively. Elemental analysis of the mixture of both the isomers of **55** also confirms the identity of the compound.



54

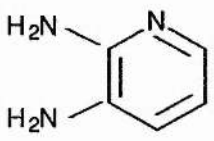


55a

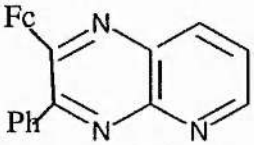
55b

3.1.1.4 Reaction of 40a with 2,3-diaminopyridine.

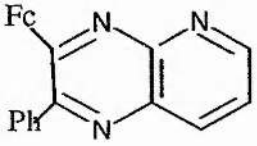
A quinoxaline-type moiety having another nitrogen in the second ring called azaquinoxaline (triazanapthalene) can be formed by the cyclocondensation of 2,3-diaminopyridine and a 1,2-diketone. Two regio-isomers namely 2-ferrocenyl-3-phenyl-5-azaquinoxaline **57a** and 3-ferrocenyl-2-phenyl-5-azaquinoxaline **57b** were formed when the cyclocondensation of 2,3-diaminopyridine **56** was carried out with ferrocenylphenyl-1,2-diketone **40a**. The two isomers which were not separable on a silica gel column, were found to be separable on alumina provided that pure dichloromethane was employed as eluent: even the slightest increase in the polarity of the mobile phase caused the isomers to elute together. The relative ratio of the two isomers in this case was calculated by the integration of ferrocene protons and was found to be *ca.* 1:1. The ^{1}H spectrum in the ferrocene region had peaks representative of a monosubstituted ferrocene, and the aromatic region integrates for eight hydrogens for both the isomers. The ^{13}C spectrum is also satisfactory and represents eleven aromatic and four ferrocene carbons for each isomer. Elemental analysis confirms the constitution of the pure compound.



56



57a



57b

3.1.1.5 Regio-selectivity in the reactions of ferrocenyl-phenyldiketone with the aromatic diamines.

In the quinoxaline-forming condensations involving substituted diamines and ferrocenylphenyldiketone **40a**, the modest regio-selectivity is determined by the relative nucleophilicities of the two amino groups in

the diamine component, and the relative electrophilicities of the two carbonyl carbon atoms in the diketone. It is assumed that the more nucleophilic amino group reacts faster with the more electrophilic carbonyl. In diamines **50** and **52**, in which an electron-withdrawing substituent is present, the amino group *meta* to the substituent will be the more nucleophilic, while the carbonyl adjacent to the phenyl ring in **40a** will be the more electrophilic, because of the strong electron-donating character of the ferrocenyl fragment. Hence, it is to be expected that **51a** is the more abundant isomer of **51**; similarly for the quinoxaline **53**, the ferrocenyl fragment is preferentially *para* to the deactivating substituent. In 2,3-diaminotoluene, the amino group *ortho* to methyl is the more nucleophilic, so that **55b** is expected to predominate, while the strong deactivation of the 2-amino group in 2,3-diaminopyridine **56** leads to the expectation of **57b** as the major isomer.

3.1.1.6 Crystal and molecular structure of compound 53.

Ferrocenylphenylnitroquinoxaline **53** after purification by alumina column was crystallized from the ethylacetate solution by slow evaporation, and single-crystal X-ray crystallography was carried out. Although all possible care was taken to isolate the single isomer of the compound, the structure obtained proved to be in fact 5:1 mixture of the two isomers with 3-ferrocenyl-2-phenyl-6-nitroquinoxaline **53a** (called isomer I in this discussion) as the major constituent and 2-ferrocenyl-3-phenyl-6-nitroquinoxaline **53b** (called isomer II in this discussion) as the minor constituent.

The structure was solved readily via the heavy-atom method, but when all the atoms were included, there were still six significant peaks (of size 0.7 to 1.0 e/Å^{-3}) in a difference map, three each in the neighbourhood of C8 and C48 of the two independent molecules. Although considerable care via chromatography was taken to try to ensure that the sample was a single isomer, it was soon realised that these additional peaks were consistent with small amount of 2-ferrocenyl-3-phenyl-6-nitoquinoxaline being present in addition to the major component 3-ferrocenyl-2-phenyl-6-nitroquinoxaline. The position of these minor occupancy nitro groups also showed that the quinoxaline framework of the minor isomers did not overlap exactly the sites of the major isomer. Fortunately, the structure of parent 2-ferrocenyl-3-phenylquinoxaline was already determined[2] and it was straightforward to take the quinoxaline coordinates from that structure and use those as a template in structural refinement.

The mixture of **53** crystallized in the triclinic system; space group P$\bar{1}$, with two molecules in the asymmetric unit. Both molecular sites in the asymmetric unit proved to contain a mixture of the two isomers with ratios derived from the refined site-occupation factors of 0.813(3):0.187(3) for molecule I (containing Fe1) and 0.860(3):0.140(3) for molecule II (containing Fe2). At each site, the location of the ferrocenyl and phenyl fragments were identical for the major and minor isomers, but the orientation of the quinoxaline fragments differed for the two isomers (*Figure 3.2*) The refinement of isomer II was subject to constraints and all the discussion of molecular geometry is therefore confined to isomer I (the major isomer in the crystal).

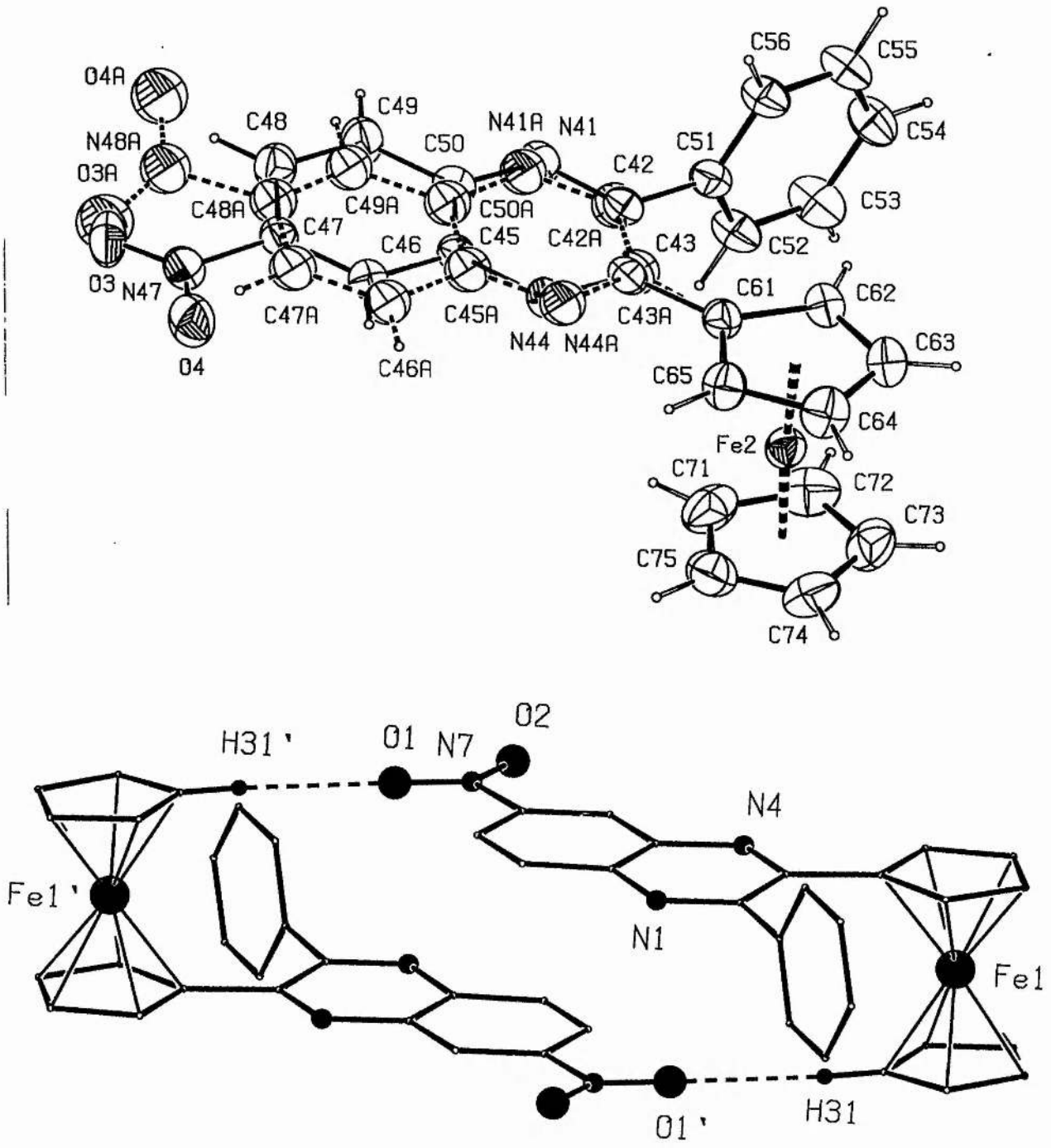


Figure 3.2 *Single crystal X-ray structure of ferrocenyl-phenyl-nitro-quinoxaline* ***53****; (top) view of the molecule with our numbering scheme, atoms from the minor isomer co-crystallized with major isomer are also visible in the nitro and the quinoxaline moieties; (bottom) hydrogen bonding between the two molecules to form* $R_2^2(22)$ *dimer.* (adapted from referrence 15)

Within the fully eclipsed ferrocene fragment, the mean C-C bond distances for the substituted and unsubstituted rings are 1.416(13) and 1.392(9) Å respectively. In molecule 1, the Fe1-Cg1 and Fe1-Cg2 distances are 1.637(2) and 1.642(2) Å respectively, with an angle Cg1-Fe1-Cg2 of 176.1(1)°, while in molecule 2 the corresponding values of Fe2-Cg3, Fe2-Cg4 and Cg3-Fe2-Cg4 are 1.641(1) Å, 1.649(1) Å and 176.2(1)° (Cg1 - Cg4 represent the centroids of the cyclopentadienyl rings C2n, C3n, C6n and C7n respectively, n = 1 - 5). For the unsubstituted rings C3n and C7n, the displacement parameters indicate significant torsional motion about the local five-fold axes. The quinoxaline fragments show marked bond fixation of the napthalene type (Appendix VIII; table 2), as observed in both ferrocenylquinoxaline[1,2] and hexachloroquinoxaline.[7] The internal angles at nitrogen (Appendix VIII; table 2) are all significantly less than 120°, as typically found in simple pyrazines and quinoxalines.

The overall molecular conformation is very similar to that found in 2-ferrocenyl-3-phenylquinoxaline.[2] In each of the two independent molecules, the quinoxaline fragment is almost coplanar with the substituted cyclopentadienyl ring, with interplanar angles of 2.0(2) and 3.4(3)° in molecules 1 and 2 respectively: similarly the nitro groups are almost coplanar with the quinoxaline rings, with interplanar angle of 2.5(3) and 8.5(4)°. By contrast the phenyl rings make interplanar angles with the quinoxaline rings of 88.2(1) and 87.8(1)° respectively.

The molecules of (isomer I) are linked into cyclic centrosymmetric dimers by a combination of C-H···O hydrogen bonds and π–π stacking interactions(Appendix VIII; table 3 anf Figure 3.2). Atom C31 in the

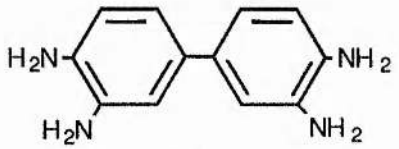
unsubstituted cyclopentadienyl ring of molecule 1 at (x, y, z) acts as donor to O1 in molecule 1 at (1 - x, 1 - y, 2 - z), so generating an $R^2_2(22)$ motif[8] for the dimer centred at (0.5, 0.5, 1.0). The corresponding atom C71 in molecule 2 at (x, y, z) acts as donor towards O3 in molecule 2 at (-x, 2 - y, 1 - z), so generating a second $R^2_2(22)$ motif for the dimer centred at (0, 1.0, 0.5). The two types of cyclic dimer thus pack to form a pseudo-CsCl type structure. Entirely similar C-H···O hydrogen bonds are formed by isomer (II), with O1A and O3A (whose positions are very close to those of O1 and O3 respectively) as acceptors (Appendix VIII; Table 3). The C-H···O hydrogen bonds are all nearly linear: in each case the H···O and C···O distances and the C-H···O angle indicate that these are fairly strong examples for their types. In addition, the two overlapping quinoxaline units in each dimer exhibit π–π stacking interactions, with interplanar separations of 3.51 and 3.52Å in the dimers formed by molecules 1 and 2 respectively. The phenyl groups appear to play no role in the dimer formation.

It is of interest to compare the structure of (I) with those of closely-related ferrocene derivatives each containing one of the two supramolecular synthons[9] evident in (I). Thus neither 2-ferrocenyl-quinoxaline[1] nor 2-ferrocenyl-3-phenylquinoxaline[2] exhibits any $\pi-\pi$ stacking interactions while 4-nitrophenylferrocene[10] exhibits no C-H···O hydrogen bonding. However, when both of these supramolecular synthons are present, as in (isomer I), supramolecular dimerisation of the ferrocenylnitroquinoxaline occurs. The effective cooperation of these two synthons in isomer I is almost certainly associated with the fact that the

typical inter-plane spacing in π–π stacked aromatic systems is very similar to the inter-ring separation in ferrocenes (Figure 3.2).

3.1.2 Ferrocene-containing bis-quinoxalines.

A step further towards polymer synthesis, condensation was carried out between a bifunctional aromatic amine, 3,3',4,4'-biphenyltetramine **58** and monofunctional ferrocenyl diketone, ferrocenylphenyl-1,2-diketone, **40a**, in another reaction bifunctional ferrocenyl diketone, ferrocene-1,1'-diylbis(phenylethanedione) **48** and monofunctional 1,2-diamine, 1,2-diaminobenzene **49** were also condensed together to give ferrocene-containing bisquinoxalines.



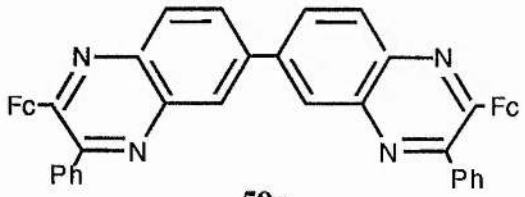
58

3.1.2.1 Reaction of 40a with 3,3',4,4'-biphenyltetramine.

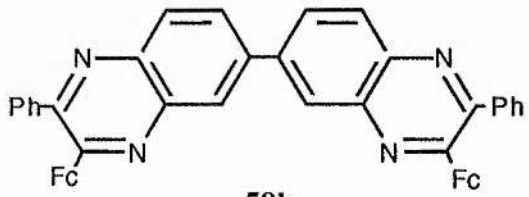
The condensation of 3,3',4,4'-biphenyltetramine **58** and **40a** in the molar ratio of 1:2 was carried out in dioxane solution as well as in aqueous ethanol containing some K_2CO_3 to help the availability of free-amine: three regio-isomers of bisquinoxalyl compound namely 2,2'-diferrocenyl-3,3'-diphenyl-6,6'-diquinoxaline **59a,** 2,2'-diphenyl-3,3'-diferrocenyl-6,6'-diquinoxaline **59b,** and 2,3'-diferrocenyl-3,2'-diphenyl-6,6'-diquinoxaline **59c**, were the expected product. The TLC shows the presence of the two purple products of very close R_f, and it is assumed that two of these isomers are appearing at the same position. Of the proposed isomers, **59a** and **59b** both have two-fold symmetry while **59c**

lacks any symmetry, and this may be the reason that the quinoxalyl product is appearing as two spots i.e. those having two fold symmetry may be behaving similarly on TLC. These isomers were not found separable either on silica gel or on alumina. However, elemental analysis and NMR studies of the isomeric mixture of the quinoxaline confirms the identity of the product as **59**. The ^{1}H NMR spectrum revealed the relative ratio of the three isomers as 9:6:5, by examining the integration of the ferrocene region, and use of resolution enhancement technique in the ^{13}C NMR spectrum enabled resolution of all 36 peaks in the aromatic region. The ferrocenyl region was also readily characterised with few peak overlaps.

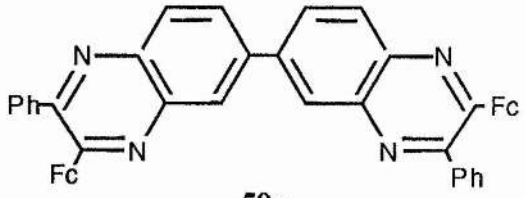
The bisquinoxalyl product in above reaction was also accompanied with the two isomers of monoquinoxalyldiamine **60** as a minor product, an intermediate in the reaction pathway. To confirm the identity of the intermediate, a reaction in the aqueous ethanol was carried out using excess **58**, where both isomers of product **60** were isolated in good yield and characterised by NMR and elemental analysis along with only traces of **59**.



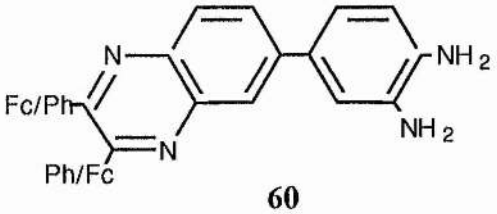
59a



59b



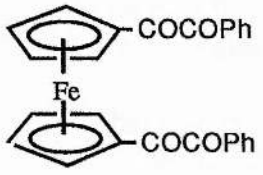
59c



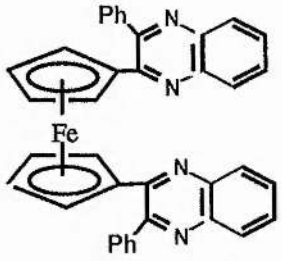
60

3.1.2.2 Reaction of 48 with 1,2-diaminobenzene.

When the bifunctional ferrocenyl diketone, ferrocene-1,1'-diylbis-(phenylethanedione) **48** and the monofunctional 1,2-diamine, 1,2-diaminobenzene **49** were reacted in the molar ratios of 1:2 respectively a bis-quinoxalyl compound, 1,1'-bis(3-phenyl-2-quinoxalyl)ferrocene **61** was the only product. The reaction was carried out in aqueous ethanol in the presence of K_2CO_3 and Na_2SO_3 in order to have the free-amine available.



(48)



(61)

The reaction was followed by TLC, early in the reaction, two new spots of different R_f appeared on the TLC. The lower R_f value spot, possibly corresponding to condensation of the diketone in one ring, disappeared slowly during the reaction, leaving only one spot. The product **61** was purified on silica gel column: the diamine in this reaction is unsubstituted hence there is no possibility of having regioisomers of this compound. The compound was crystallized from dichloro-methane/diethylether, to produce red, thin plate like crystals suitable for single-crystal X-ray analysis. The X-ray structure showed 0.9 mol of dichloromethane present in the crystal lattice, hydrogen bonded to a quinoxaline nitrogen. The ^1H NMR spectrum shows two peaks of equal

intensity arising from two sets of CH protons in Cp rings in the ferrocene region, which integrate for 4 protons each, while the phenyl region integrates for 18 protons. The ^{13}C spectrum shows three non equivalent ferrocenyl carbons including one quaternary carbon and the aromatic region shows all 12 carbons of which 5 are quaternary. Elemental analysis when calculated for $C_{38}H_{26}FeN_4.0.9CH_2Cl_2$, as revealed from X-ray analysis was found to be satisfactory. The X-ray structure of 1,1'-bis(3-phenyl-2-quinoxalyl)-ferrocene **61** is shown in *Figure 3.4*; and section 3.1.2.3 contains a discussion of its crystal structure.

3.1.2.3 Crystal and molecular structure of compound 61.

Compound **61** crystallized from diethylether/dichloromethane as a partial dichloromethane solvate,$C_{38}H_{26}FeN_4.0.9CH_2Cl_2$, in which the solvent molecule is hydrogen-bonded to one of the quinoxaline fragments by means of a C-H···N hydrogen bond (Figure 3.3). Within the molecules of compound **61** the Fe-Cg1 and Fe-Cg2 distances are 1.656(1) and 1.655(1) Å and the Cg1-Fe-Cg2 angle is 177.8(1)°; (Cg1 and Cg2 represent the centroids of the cyclopentadienyl rings C1n and C2n respectively, for n = 1 - 5). The mean value of the C-C bond distances in these rings is typical of those observed in other mono-substituted ferrocenylquinoxalines.[1,2] The quinoxalinyl fragments in **61** both exhibit the bond fixation typical of the heteroaromatic system.[1,2,7] The conformation of **61** and the molecular packing are intimately connected. The independent quinoxalinyl groups are both nearly coplanar with the neighbouring cyclopentadienyl ring, with interplanar angles between quinoxalinyl and cyclopentadienyl rings of 5.2(3) and 7.8(3)° for the

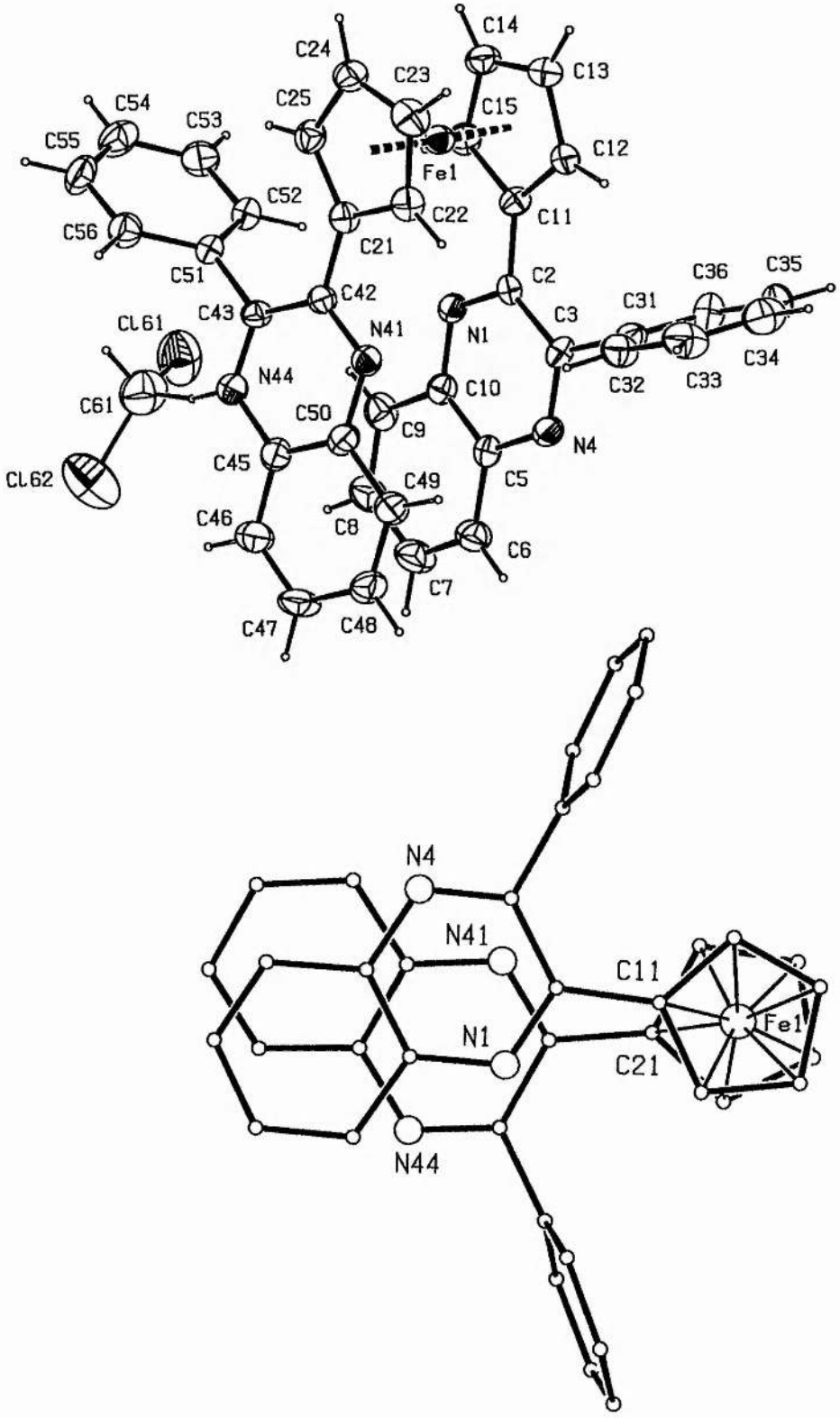


Figure 3.3 *Single crystal X-ray structure of 1,1'-bis(3-phenyl-2-quinox-alyl)-ferrocene* ***61*** *(top) view of the molecule with our numbering scheme (bottom) view from the top of the molecule* (adapted from reference 16)

fragments containing C11 and C21 respectively, while the dihedral angles between the two quinoxalinyl planes is 5.4(2)°. Moreover, the mean value of the torsion angles C1n-Cg1-Cg2-C2n (n = 1 - 5) is -20.9(9)°, where a value of zero would indicate perfect eclipsing of both the cyclopentadienyl rings and the exocyclic C-C bonds: consequently the two independent quinoxalinyl groups within the molecule exhibit considerable overlap (Figure 3.3). The mean perpendicular distance between the groups is ca, 3.4Å, so that intramolecular π–π stacking interactions are significant, and indeed are possibly the dominant factor underlying the observed conformation: this is almost certainly associated with the fact that the typical inter-plane spacing in π–π stacked aromatic systems is very similar to the inter-ring separation in ferrocenes. Furthermore, adjacent molecules are stacked in columns along the [100] direction, such that there are intermolecular π–π stacking interaction between the C2n ring in the molecule at (x, y, z) and the 10-membered heteroaromatic ring containing N1 and N4 at (-1 + x, y, z), with a mean perpendicular distance between these rings of ca. 3.5Å, so that the intra- and inter-molecular spacings are very similar. As in 2-ferrocenyl-3-phenylquinoxaline,[2] the neighbouring phenyl and quinoxalinyl groups are nearly normal to one another: the twists of the phenyl groups (76.5(1), 77.0(1)° away from co-planarity with the quinoxalinyl groups is forced by the presence of the adjacent bulky ferrocenyl group.

3.1.3 Electrochemical study of ferrocene-containing quinoxalines.

Figure 3.4, which refers to compound **7**, shows the typical cyclic voltammogram exhibited by the present compounds in dichloromethane

solution. Both an oxidation process possessing features of chemical reversibility and an apparently irreversible reduction process, which is about twice greater in height than the oxidation step, are apparent.

Controlled-potential coulometric investigation of the anodic process (E_W = +0.7 V) show the consumption of one electron/molecule. Upon exhaustive one-electron oxidation the original ruby-red solution of **7** turns jade-green and displays an absorption in the visible region at λ_{max} = 692 nm, which supports an iron-centred anodic step. In confirmation of

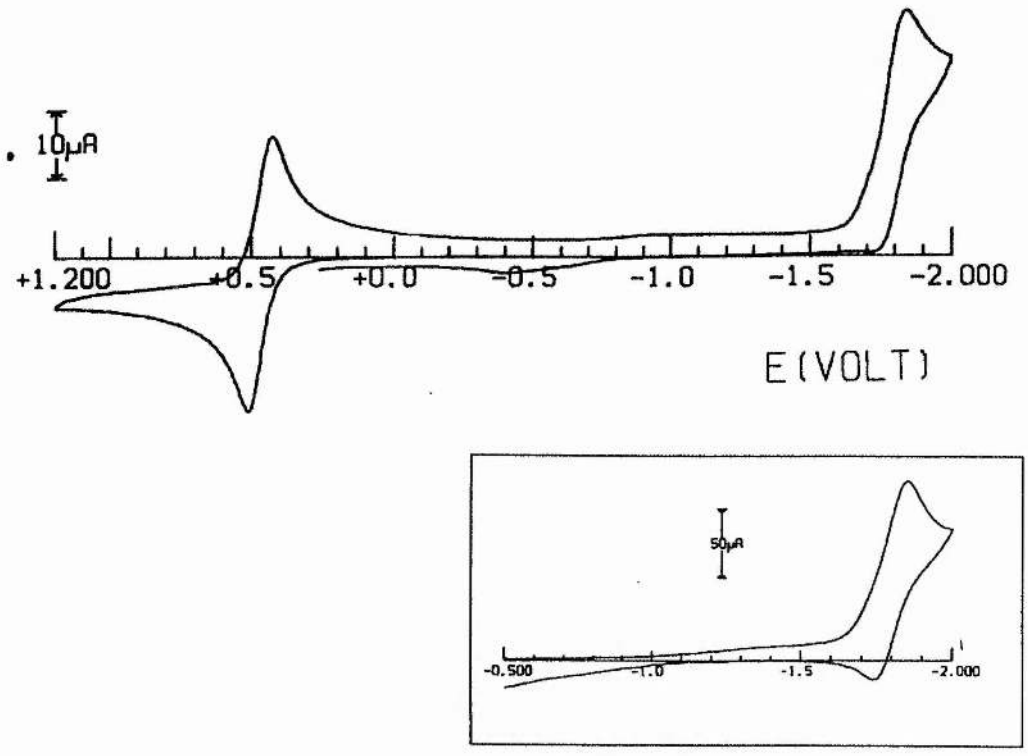


*Figure 3.4 Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution containing **7** ($1.3x10^{-3}$ mol dm^{-3}) and $[NBu_4][PF_6]$ (0.2 mol dm^{-3}). Scan rates: main figure, 0.20 V s^{-1}; inset, 2.00 V s^{-1}.*

the chemical reversibility of the ferrocene/ferricenium oxidation, cyclic-voltammetric tests performed on the oxidised green solution display voltammetric profiles entirely complementary to that shown in Figure 3.4.

Analysis of the cyclic-voltammetric anodic responses with scan rates varying from 0.02 V s^{-1} to 1.00 V s^{-1} show parameters which are diagnostic of a one-electron removal which is essentially reversible from the electrochemical viewpoint. As a matter of fact, the i_{pc}/i_{pa} ratio is constantly equal to unity, the current function $i_{pa}/v^{1/2}$ remains constant, and the peak-to-peak separation progressively increases from 70 to 97 mV. Such a slightly departure from the constant value of 59 mV expected for an electrochemically-reversible one-electron process neatly parallels that observed for the one-electron oxidation of unsubstituted ferrocene, so that it may be attributed to uncompensated solution resistances.

So far as the reduction process is concerned, it was not possible to perform macroelectrolysis investigations because of the closeness of the solvent reduction. Based on the relative heights, we assign it to a single two-electron reduction process, which is however complicated by subsequent reactions, as yet uncharacterised. As the inset of Figure 3.4 shows, when the scan rate was increased beyond 2.00 V s^{-1}, a reoxidation appears directly associated to the reduction process. This means that the rate of the chemical complication falls within the cyclic voltammetry time window,[11] allowing estimation of ca. 0.05 s as the half-life of the electrogenerable anion $[\mathbf{7}]^{2-}$.

Table 3.1 presents for all the compounds studied the formal electrode potentials of the redox changes discussed above, and for comparison, the corresponding data for the unsubstituted 2-ferrocenylquinoxaline[12] **6** are also reported. The electrogenerated ferricenium species $[\mathbf{51}]^+$, $[\mathbf{57}]^+$ and $[\mathbf{6}]^+$ proved to be not fully stable and to undergo slow decomposition.

In comparison with unsubstituted ferrocene itself, the ferrocenylquinoxalines oxidise at potential values some 100 - 150 mV higher , thus indicating that the quinoxaline exerts a significant electron-withdrawing effect. However, the effects of the substituents on the quinoxaline ring are always readily interpreted. Comparison between **6** and **7**, indicates that the 3-phenyl substituent, which might have been expected to make the oxidation more difficult, in fact makes the oxidation slightly easier, suggesting that resonance effects predominate over inductive effects. This could also explain the absence of inductive effects exerted by the methyl group in **55**, or the carboxyl group in **51**, compared with **7**. On the other hand, the strongly electron-withdrawing NO_2 group in **53** generates its expected effect.

The redox behaviour of the biferrocene complex **59** merits comment. It exhibits a single oxidation process, but unfortunately, because of its very low solubility satisfactory controlled-potential coulometry was not possible. However, in view of the absence of further oxidation processes up to +1.2 V, it may be speculated that this is due to a single two-electron step. Were this to be so, it would imply that no electronic communication occurs between the two quinoxalyl units.

Finally, as far as the presence of isomeric species is concerned, as noted above for compounds **51, 53, 55, 57** and **59**, it may be pointed out that only in the case of compound **51** was the presence of two almost overlapping oxidation processes observed, which could account for the somewhat greater peak-to-peak separation in **51** compared with the other species.

Table 3.1 Formal electrode potentials (in Volt, vs. S.C.E.), peak-to-peak separations (in mV), and spectroscopic data (in nm) for the redox changes exhibited by some ferrocenylquinoxalines in dichloromethane solution.

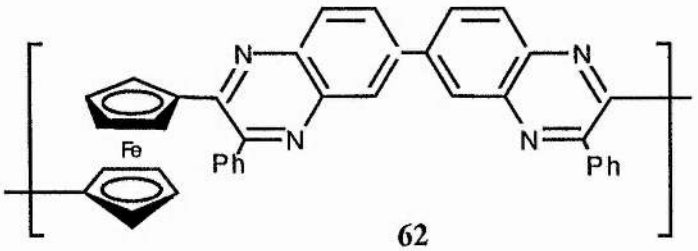
Compounds	$E^{\circ\prime}_{0/1+}$	ΔEp^{a}	$\lambda_{max}{}^{b}$	$E^{\circ\prime}_{0/2-}$
6	+0.53	95	675	-1.79[d]
7	+0.47	80	692	-1.80[c]
51	+0.49	97	680	-
53	+0.55	75	660	-1.55[d,e]
55	+0.49	79	705	-1.80[d]
57	+0.55	75	681	-1.51[c]
59	+0.46[f]	70	-	-
FcH	+0.39	84	620	-

[a] Measured at 0.1 V s^{-1};
[b] absorption band of the oxidised species;
[c] measured at 2.0 V s^{-1};
[d] peak potential value;
[e] a preceding reduction centred on the NO_2 group is present at $E^{\circ\prime}$ = -0.95 V;
[f] two-electron step.

3.1.4 Ferrocene-containing polyquinoxalines.

Having successfully synthesised and characterised ferrocene containing mono- and bis-quinoxalines by the cyclocondensation of mono- and bi-functional diketones and mono-and bi-functional aromatic diamines, a polycondensation reaction was carried out between the bifunctional diketone ferrocene-1,1'-diylbis(phenylethanedione) **48** and the bifunctional diamine 3,3',4,4'-biphenyltetramine **58**, to synthesise ferrocene-containing polyquinoxaline (FCPQx). When the reaction was carried out as a solution in neat chlorobenzene under nitrogen, as in previous syntheses, it was observed by TLC that the reaction was not complete even after several hours reflux. However when few crystals of *p*-toluene sulfonic acid (PTSA) were added as a catalyst, the reaction then proceeded smoothly. The product formed was found to be soluble in dichloromethane but insoluble in ethanol, contrary to mono- and bis-quinoxalines. An FTIR spectrum of the reaction mixture of **48** and **58** was run before and after the condensation reaction. The spectrum before the reaction showed two peaks of carbonyl functional-group at 1653 and 1649 cm^{-1} and four peaks at 3394, 3365, 3296 and 3199 cm^{-1} arising from amino groups. The spectrum after the condensation reaction shows no amino absorptions, and a diminished absorption in the carbonyl region indicates that the endgroups of the polymeric chain are ketonic. Another possibility of the reaction, formation of a macrocycle, can be ruled out on the basis of this observation. Although the polymer was kept in an oven at 100 °C for 48h, a very strong absortpion due to water was observed in the FTIR spectrum. That indicates the presence of water of hydration on the quinoxalinic nitrogens in the polymer chain, consistent with the

previous observations on mono- and bis-quinoxalines. NMR studies were not carried out as no further information about the reaction or chain length is expected from that. The structure of the repeating unit in the polymer is expected as **62** with ferrocenyl diketone at the end of the chain.



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3.2 EXPERIMENTAL DETAILS

NMR spectra were recorded at ambient temperatures, all ^{13}C spectra were recorded as decoupled, in $CDCl_3$ solution unless stated otherwise, on a Bruker AM-300 spectrometer operating at 300.135 MHz for ^{1}H and 75.469 MHz for ^{13}C.. Elemental analysis was carried out in the microanalytical laboratory of the School of Chemistry. Diethylether and light petroleum (b.p. 40-60 °C) were dried over sodium wire, and dichloromethane was distilled over calcium hydride prior to use. All the other chemicals were used as received unless stated otherwise.

3.2.1 Synthesis of 2-ferrocenyl-3-phenylquinoxaline.

a) In melt phase:-

Ferrocenylphenyldiketone **40a** (0.2 g, 0.63 mmol) and 1,2-diaminobenzene **49** (0.1g, 0.93 mmol) were taken in a pyrex glass test tube with a side arm and fitted with a bubbler. The mixture was heated to melting in an oil bath at 140 °C under nitrogen for 30 min., and water

vapours were observed condensing on the walls of tube. After cooling the crude material was dissolved in dichloromethane and was checked by TLC; TLC showed one purplish-red spot almost at the same R_f value as ferrocenyldiketone along with a spot of 1,2-diaminobenzene at the starting point. This crude product was chromatographed on silica gel using dichloromethane as eluting solvent, concentrated and crystallized to give dark purple crystals of 2-ferrocenyl-3-phenylquinoxaline (0.11g, 44.7%).

b) In solution phase:-

Ferrocenylphenyldiketone **40a** (0.2 g, 0.63 mmol), 1,2-diamino-benzene **49** (0.1g, 0.93 mmol) and 1,4-dioxane (2 cm^3) were taken in a pyrex glass test tube with a side arm and fitted with a bubbler. The mixture was heated in an oil bath at 110 °C under a gentle stream of nitrogen until dryness. The temperature of the bath was raised to 140 °C and was kept at this temperature for 20 min. Workup is the same as above. Yield 0.16 g, 65%.

The products from these two processes were found to be identical by TLC and by ^1H and ^{13}C NMR. Anal. found C 72.2%, H 4.4%, N 6.9%; $C_{24}H_{18}FeN_2$ requires C 73.9%, H 4.7%, N 7.2%; $C_{24}H_{18}FeN_2.0.5H_2O$ requires C 72.2%, H 4.8%, N 7.0%. M.p. 208-210 °C (lit. 208-209 °C).[13]

$\delta_H(CDCl_3)$ 4.00. (5H, s, C_5H_5), 4.35 (2H, t, C_5H_4), 4.55 (2H, t, C_5H_4), 7.50 (3H, m, Ph), 7.55 (2H, m, Ph), 7.72 (2H, m, Quinox.) and 8.08 (2H, m, Quinox.).

$\delta_C(CDCl_3)$ 69.9(5, s, C_5H_5), 70.1 (2C, s, C_5H_4) 70.8 (2C, s, C_5H_4) and 82.3 (1C, s, C_5H_4), [128.4, 128.8, 128.9, 129.0, 129.2, 129.3, 129.9, 139.8, 140.3, 141.9, 154.1 and 154.1](s, Ph or Quinox).

3.2.2 Synthesis of ferrocenylphenylquinoxalylcarboxylic acid.

In a pyrex glass test tube with a side arm and fitted with a bubbler, ferrocenylphenyldiketone **40a** (0.5 g, 1.57 mmol), 3,4-diaminobenzoic acid **50** (0.26 g, 1.7 mmol) and chlorobenzene (5cm^3) were taken. The mixture was heated in a silicone oil bath at 140 °C under gentle stream of nitrogen; after 1h there was no spot of unreacted diketone on TLC. During this time the colour of the mixture also changed from dark red to dark purple. The mixture was then heated to dryness. After cooling down, the solid residue was dissolved in dichloromethane, filtered, washed with water, dried (Na_2SO_4), concentrated and chromatographed over silica gel using diethyelther as mobile phase to yield the mixture of two isomers of ferrocenylphenylquinoxalylcarboxylic acid **51** (0.55 g, 80.7 %) as a dark purple solid. The ^{1}H NMR spectrum shows the presence of both the regio-isomers. The relative yield of the regioisomers as calculated from the ^{1}H NMR integration is 1:2.

Anal. found C 66.9%, H 4.7%, N 5.7%; $C_{25}H_{18}FeN_2O_2$ requires C 69.1%, H 4.2%, N 6.5%; $C_{25}H_{18}FeN_2O_2.H_2O$ requires C, 66.4%; H, 4.5%; N, 6.2%.

NMR $\delta H(CDCl_3)$: (major isomer) 4.01 (5H, s, C_5H_5); 4.38 (2H, m) and 4.58 (2H, m) (C_5H_4); 7.4 - 7.7 (5H, m, Ph); 8.15 (1H, d J 8.8), 8.35 (1H, dd, J 8.8 & 1.6) and 8.92 (1H, d, J 1.6) (quinoxalyl);. (minor isomer) 4.03 (5H, s, C_5H_5); 4.40 (2H, m) and 4.60 (2H, m) (C_5H_4); 7.4 - 7.7 (5H, m,

Ph); 8.15 (1H, d , J 8.8), 8.38 (1H, dd, J 8.8 & 1.6) and 8.91 (1H, d, J 1.6) (quinoxalyl);

δC($CDCl_3$+DMSO) (major isomer) 68.47(d, C_5H_5); 69.0(d), 69.5(d) and 80.1 (s) (C_5H_4); (minor isomer) 68.5_3(d, C_5H_5); 69.3(d), 69.6(d) and 80.4 (s) (C_5H_4); (both isomers) 126.9_3(d), 126.9_6(d), 127.0_5(d), 127.1_6(d), 127.6_3(d), 127.7_2(d), 127.7_8(d), 128.3(d), 129.6(d), 129.8(d), 130.1(d), 131.1(d), 137.3(s), 138.1_7(s), 138.2_4(s), 139.4(s), 140.0(s), 142.0(s), 152.4(s), 153.0(s), 153.6(s) and 154.6(s) (phenyl and quinoxalyl); 166.2(s) COOH. The resolution of the aromatic resonances requires resolution enhancement. Both the carboxylic carbons appear at the same position, and two of the quaternary carbons of the aromatic/quinoxaline moieties are superimpose on other peaks in that region and hence are not visible in the spectrum.

3.2.3 Synthesis of ferrocenylphenylnitroquinoxaline.

In a pyrex glass test tube with a side arm and fitted with a condenser, ferrocenylphenyldiketone **40a** (0.22 g, 0.69 mmol), 4-nitro-1,2-diaminobenzene **52** (0.12 g, 0.76 mmol) and toluene ($5cm^3$) were refluxed under gentle stream of nitrogen for 3h, while the reaction was monitored by the Tlc, the solvent was evaporated after this time. After cooling down, the solid residue was dissolved in dichloromethane, filtered, concentrated and chromatographed over silica gel using dichloromethane as mobile phase to yield the mixture of two isomers of ferrocenylphenylnitroquinoxaline **53** (0.22 g, 73.2%) as a dark purple solid. NMR spectra show the presence of both the regio-isomers. The relative yield of the regioisomers as calculated from the ^1H NMR integration in the ferrocene region is 1:3.

Anal. found (isomer mixture) C 65.1%, H 3.9%, N 9.1%; $C_{24}H_{17}FeN_3O_2$ requires C 66.2%, H 3.9%, N 9.6%; $C_{24}H_{17}FeN_3O_2.0.5H_2O$ requires C 64.9%, H 4.1%, N, 9.4%. NMR (major isomer pure, minor isomer from spectrum of mixture) δ(H) (major isomer) 4.01 (5H, s, C_5H_5); 4.40 (2H, m) and 4.57 (2H, m) (C_5H_4); 7.5 - 7.6 (5H, m, Ph); 8.18 (1H, d, J 9.5), 8.44 (1H, dd, J 9.5 & 2.4) and 8.98 (1H, d, J 2.4) (quinoxalyl); (minor isomer) 4.00 (5H, s, C_5H_5); 4.43 (2H, m) and 4.60 (2H, m) (C_5H_4); 7.5 - 7.6 (5H, m, Ph); 8.16 (1H, d, J 9.4), 8.48 (1H, dd, J 9.4 & 2.4) and 8.98 (1H, d, J 2.4) (quinoxalyl); δ(C) (major isomer) 69.9 (d, C_5H_5); 70.8(d), 71.1(d) and 80.8 (s) (C_5H_4); 121.8(d), 124.7(d), 128.4(d), 128.9_0(d), 129.5(d), 130.5(d), 138.9(s), 140.4(s), 142.0(s), 147.9(s), 144.8(s) and 157.1(s) (phenyl and quinoxalyl); (minor isomer) 70.0 (d, C_5H_5); 71.2_5(d), 71.2_8(d) and 80.7 (s) (C_5H_4); 123.2(d), 125.6(d), 128.2(d), 128.8_7(d), 129.4(d), 129.6(d), 138.0(s), 138.9(s), 144.1(s), 146.7(s), 145.2(s) and 158.1(s) (phenyl and quinoxalyl).

3.2.4 Synthesis of ferrocenylphenylmethylquinoxaline.

In a pyrex glass test tube with a side arm and fitted with a condenser, ferrocenylphenyldiketone **40a** (0.5 g, 1.57 mmol), 2,3-diaminotoluene **54** (0.22 g, 1.8 mmol) and chlorobenzene ($5cm^3$) were refluxed in an oil bath at 150 °C under gentle stream of nitrogen. The reaction was monitored by Tlc; after 4h the reaction was judged to be complete. Both the regio-isomers were observed at different places on Tlc, the less polar isomer appeared at almost the same place as the diketone, sometimes it was difficult to differentiate between diketone and this isomer of the product, however a mixed Tlc of the reaction mixture and the diketone was helpful in differentiating the two. After the reaction was completed,

the solvent was evaporated, the solid residue was dissolved in dichloromethane, filtered, concentrated and chromatographed over silica gel using dichloromethane/petrol as mobile phase to yield a mixture of the isomers of ferrocenylphenylmethylquinoxaline **55** (0.6 g, 94.5 %) as a dark purple solid. The relative yield of the regio-isomers as calculated from the ^{1}H NMR integration was 3:2. Another column was run to separate the two isomers from each other, that yielded the pure less-polar fraction first and then the mixture of the two isomers and then finally a small portion of the relatively more polar fraction.

Anal. found C, 74.0%; H, 5.0%; N, 6.7%; $C_{25}H_{20}FeN_2$ requires C, 74.3%; H, 5.0%; N, 6.9%.

NMR data for the more polar, major isomer:

$\delta_H(CDCl_3)$ 2.95 (3H, s, CH_3) 4.02 (5H, s, C_5H_5), 4.32 (2H, t, C_5H_4), 4.55 (2H, t, C_5H_4), [7.45-7.66 (7H, m), 7.94 (1H, d) Ph and Quinox.].

$\delta_C(CDCl_3)$ 17.11 (1C, s, CH_3), 69.68 (5C+2C, s, C_5H_5,C_5H_4) [70.79 (2C, s), 82.95 (1C, s, *ipso*)](C_5H_4), [126.76 (1C), 128.12 (2C), 128.50 (1C), 128.55 (1C), 129.11 (2C), 129.45 (1C), {136.49, 139.59, 139.79, 140.76, 152.13, 152.35} (*ipso*)] (s, Ph or Quinox.).

NMR data for the less polar, minor isomer:

$\delta_H(CDCl_3)$ 2.82 (3H, s, CH_3) 4.00 (5H, s, C_5H_5), 4.32 (2H, t, C_5H_4), 4.55 (2H, t, C_5H_4), [7.45-7.66 (7H, m), 7.94 (1H, d) Ph and Quinox.].

$\delta_C(CDCl_3)$ 17.02 (1C, s, CH_3), 69.60 (5C+2C, s, C_5H_5,C_5H_4) [70.70 (2C, s), 82.72 (1C, s, *ipso*)](C_5H_4), [126.21 (1C), 127.92 (2C), 128.44 (1C), 128.60 (1C), 129.22 (1C), 129.41 (2C), {137.27, 138.80, 140.18, 141.38, 151.41, 152.88} (*ipso*)] (s, Ph or Quinox.).

3.2.5 Synthesis of ferrocenylphenylazaquinoxaline.

Ferrocenylphenyldiketone **40a** (0.32 g, 1.0 mmol), 2,3-diaminopyridine **56** (0.22g, 2.0 mmol) and 1,4-dioxane (2 cm^3) were taken in a pyrex test tube with side arm and fitted with bubbler. The assembly was heated in an oil bath at 110 °C under a gentle stream of nitrogen until all the solvent had been lost. The temperature was then raised to 150 °C and was held for 30 min. After cooling, the mixture was dissolved in dichloromethane, filtered, concentrated to minimum volume and chromatographed on a silica gel column to give the two isomers of pure ferrocenylphenylazaquinoxaline **57** (0.26 g, 66.5 %) as a dark purple solid. The two isomers which were not separable on silica gel were found to be separable on neutral alumina by very careful and time consuming elution using pure dichloromethane. The slightest increase in the polarity of the mobile phase causes the elution of both the isomers at the same time. The relative ratio of the two isomers as judged from the integaration of the ^1H spectrum was *ca.* 1:1.

Anal. found C, 69.8%; H, 4.6%; N, 10.1%; $C_{23}H_{17}FeN_3$ requires C, 70.6%; H, 4.4%; N, 10.7%; $C_{23}H_{17}FeN_3.0.5H_2O$ requires C, 69.0%; H, 4.5%; N, 10.5%.

NMR data for the less abundant isomers:

$\delta_H(CDCl_3)$ 4.06 (5H, s, C_5H_5), 4.40 (2H, t, C_5H_4), 4.68 (2H, t, C_5H_4), 7.40-7.78 (6H, m, Ph and Quinox.), 8.46 (1H, d of d, Quinox.), 9.15 (1H, d, Quinox.).

$\delta_C(CDCl_3)$ 69.75 (5C, s, C_5H_5), [70.73 (2C, s), 71.03 (2C, s), 80.52 (1C, s, *ipso*)](C_5H_4), [123.73, 128.17, 128.72, 128.93, 134.18 (*ipso*), 137.71,

139.19 (*ipso*), 150.00 (*ipso*), 153.60, 154.10 (*ipso*), 157.81 (*ipso*)](s, Ph or Quinox).

NMR data for the more abundant isomer:

$\delta_H(CDCl_3)$ 4.02 (5H, s, C_5H_5), 4.38 (2H, t, C_5H_4), 4.62 (2H, t, C_5H_4), 7.45-7.72 (6H, m, Ph and Quinox.), 8.42 (1H, d of d, Quinox.), 9.10 (1H, d, Quinox.).

$\delta_C(CDCl_3)$ 69.61 (5C, s, C_5H_5), [70.15 (2C, s), 70.83 (2C, s), 81.83 (1C, s, *ipso*)](C_5H_4), [124.80, 127.81, 128.93, 129.18, 136.23 (*ipso*), 136.84, 138.77 (*ipso*), 148.37 (*ipso*), 152.45, 155.34 (*ipso*), 155.54 (*ipso*)](s, Ph or Quinox).

3.2.6 Synthesis of bis(ferrocenylphenylquinoxaline).

In dioxane.

In a pyrex glass test tube with a side arm and fitted with a bubbler, ferrocenylphenyldiketone **40a** (0.3 g, 0.94 mmol), 3,3',4,4'-biphenyltetramine **58** (0.1 g, 0.467 mmol) and 1,4-dioxane (2 cm^3) were taken. The mixture was heated in an oil bath at 110 °C under gentle stream of nitrogen until all the solvent had been lost. The temperature of oil bath was then raised to 150 °C and mixture was kept at this temperature for 1 h. After cooling down, the solid residue was dissolved in dichloromethane and chromatographed to yield (54%) bis(ferrocenylphenylquinoxaline) **59**.

In aqueous ethanol.

Ferrocenylphenyldiketone **40a** (0.4g, 1.26 mmol), 3,3',4,4'-biphenyltetramine **58** (0.13 g, 1.9 mmol), potassium carbonate (0.2g) and sodium sulfite (0.4g) were taken in a 250 cm^3 round bottom flask and 1:1 mixture (100 cm^3) of ethanol-water was added. The mixture was refluxed

under nitrogen for 5h. After the lapse of time the mixture was cooled to room temperature. The precipitated product was filtered off and the product was extracted in dichloromethane from the reaction mixture. The combined product was chromatographed to yield 63.2% of pure **59** accompnied with 6.4% of monoquinoxaline product **60.**

In both the cases, products on Tlc analysis showed the presence of two purple quinoxaline spots. As three regio isomers wre expected from this reaction, (**59a, 59b, 59c**) it is presumed that two of these isomers are appearing at the same place. These isomers were found unseparable on silica gel as well as alumina column. However, integration of the ^{1}H NMR spectrum of the mixture of **59** confirms the presence of the three isomers with a relative ratio of 9:6:5, ^{13}C NMR also confirms the presence of all three isomers of compound **59**.

Anal.(mixture of three isomers) found C 73.1%, H 4.1%, N 7.0%; $C_{48}H_{34}Fe_2N_4$ requires C 74.1%, H 4.4%, N 7.2%; $C_{48}H_{34}Fe_2N_4.0.5H_2O$ requires C 73.2%, H 4.5%, N 7.1%.

$\delta_H(CDCl_3)$ 4.05 (3 x 5H, 3 x s, C_5H_5), 4.35 (3 x 2H, m, C_5H_4), 4.58 (3 x 2H, m, C_5H_4), 7.45-8.56 (3 x 8H, m, Ph and Quinox.).

$\delta_C(CDCl_3)$ 69.82 (5C, s, C_5H_5), (69.86, 70.17, 70.24, 70.27, 70.84, 70.86, 82.08 *ipso*, 82.14 *ipso*) (C_5H_5 or C5H4), (126.57, 126.72, 126.90, 127..01, 127.29, 128.01, 128.14, 128.19, 128.34, 128.52, 128.66, 128.88, 129.10, 129.13, 129.22, 129.33, 129.70, 129.74, 130.13, 139.28, 139.78, 139.81, 139.90, 140.14, 140.18, 141.19, 141.28, 141.85, 144.64, 153.25, 153.30, 153.72, 154.20, 154.30, 154.65, 154.69 (s, Ph or Quinox.). The appearence of some of the peaks above requires resonance enhancement technique.

3.2.7 Synthesis of ferrocenyl-phenyl-6-(3',4'-diaminophenyl)-quinoxaline.

Ferrocenylphenyldiketone **40a** (0.10 g, 0.314 mmol), 3,3',4,4'-biphenyltetramine **58** (0.13g, 0.61 mmol), sodium sulfite (0.06g, 0.48 mmol) and potassium carbonate (0.06g, 0.43 mmol) were dissolved in 1:1 aqueous ethanol (50 cm^3). The mixture was refluxed with stirring for 2 h. After this time, TLC of the organic extract showed two highly polar components of very similar R_f values, in addition to traces of the bis-quinoxaline **59** and unreacted biphenyltetramine. During the course of the reaction some solid product precipitated out; this was filtered off and the filtrate extracted with diethyl ether. The combined solids were purified by chromatography on neutral alumina using 20% (v/v) methanolic diethylether as eluent to yield the two isomers of ferrocenyl-phenyl-6-(3',4'-diaminophenyl)quinoxaline **60** (0.12g, 77%). Anal. found C 71.6%, H 4.8%, N 11.0%; $C_{30}H_{24}FeN_4$ requires C 72.6%, H 4.9%, N 11.3%; $C_{30}H_{24}FeN_4.0.5H_2O$ requires C 71.3%, H 5.0%, N 11.1%. FTIR spectrum shows two NH absorptions at 3355 and 3414 cm^{-1}, while in starting material **58** four NH peaks were observed in that region.

3.2.8 Synthesis of 1,1'-bis(3-phenylquinoxaline-2-yl)-ferrocene.

Ferrocendiylbisdiketone **48** (0.12 g, 0.266 mmol), 1,2-diamino-benzene **49** (0.1g, 0.92 mmol), sodium sulfite (0.06g) and potassium carbonate (0.06g) were dissolved in 250 cm^3 round bottom flask in 1:1 ethanol/water mixture (50 cm^3). The mixture was stirred and refluxed for 6 h. The reaction was followed by Tlc, in the beginning two purple spots

were observed one of relatively lower Rf value; presumably monocondensed product, and the other of higher Rf value of the di condensed product. The former spot disappeared with the course of reaction. During the course of the reaction some solid product was also precipitated out that was filtered out and product was extracted from reaction mixture into dichloromethane. Solid residue and organic extract were mixed together and purification on short silica gel column using 5% diethylether/dichloromethane yielded 1,1'-bis(3-phenylquinoxaline-2-yl)ferrocene.**61** (0.14g, 88.5%).

Anal. found C, 70.8%; H, 4.2%; N, 8.4%; $C_{38}H_{26}N_4Fe$ requires C, 76.8%; H, 4.4%; N, 9.4%.$C_{38}H_{26}FeN_4.0.9CH_2Cl_2$[14] requires C, 69.6%; H, 4.2%; N, 8.4%.;

$\delta H(CDCl_3)$ 4.18 (s, 2H, $2xC_5H_4$), 4.40 (s, 2H, $2xC_5H_4$), 7.35-7.80 (m, 9H, 2x Ph or Quinox.).

$\delta C(CDCl_3)$ 71.1 (s, 2C, $2xC_5H_4$), 72.3 (s, 2C, $2xC_5H_4$), 83.8 (s, 1C, $2xC_5H_4$-*ipso*), 128.2 (s, 1C, 2xPh or Quinox.), 128.4 (s, 2C, 2xPh), 128.4 (s, 1C, 2xPh or Quinox.), 128.7 (s, 1C, 2xPh or Quinox.), 128.9 (s, 1C, 2xPh or Quinox.), 129.1 (s, 1C, 2xPh or Quinox.), 129.6 (s, 1C, 2xPh or Quinox.), [138.4, 140.2, 141.1, 151.0 and 152.9] (s, 1C, Ph or Quinox.).

3.2.9 Synthesis of ferrocene-containing polyquinoxaline.

In a 100 cm^3 round bottom flask ferrocenylphenylbisdiketone **48** (0.45g, 0.001 mol) and 3,3',4,4'-biphenyltetramine **58** (0.21g, 0.001 mol) were refluxed under nitrogen, in chlorobenzene (50 cm^3), in the presence of a few crystals of *p*-toluenesulfonic acid. The colour of the reaction mixture turned dark purple during the reaction, after 3 h. no spot for

unreacted ferrocenylphenylbisdiketone **48**, was observed on Tlc. The solvent was evaporated that yielded dark black-red solid (0.55g) FTIR spectrum of the product was obtained, that showed no aminic absorptions and residual peaks for carbonyl groups, that indicated that the end groups are ketonic functional in the ferrocene-containing polyquinoxaline (FCPQx) polymer chains.

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CHAPTER 4

FERROCENE-CONTAINING IMINES

In this chapter the condensation of ferrocenecarboxaldehyde with some aromatic amines and diamines is described to produce mono-ferrocenyl imines and di-ferrocenyl bis-imines. Condensation of 1,1'-ferrocenedicarboxaldehyde and aromatic di-amines yielded polymeric ferrocene-containing imine; the average molecular weight of the polymers have also been estimated.

4.1 RESULTS AND DISCUSSION

4.1.1 Ferrocenyl Imines.

Similar to quinoxalines, ferrocene-containing imines (sometimes also called Schiff's bases) can be synthesised by the condensation of an amine and a ferrocene-containing aldehyde or a ketone (Equation 4.1). The difference is that only one amino and one carbonyl group is required for the synthesis of a single imino unit (-CH=N-) and there is no cyclization in this case. The newly formed C=N bond is in the open chain between the two molecules; these reactions are (usually) acid catalysed contrary to the quinoxalines in which cyclization of the molecule stablises the overall product and reaction can proceed without a catalyst. Care must be taken in the choice of the acid catalyst, since if the reaction medium becomes too acidic the amino group may form a salt with the acid and there will be very little or no free amine available to participate in the reaction. Experiments have shown that a pH of *ca.* 4 is the optimum for this type of reaction,[1] and *p*-toluenesulfonic acid (PTSA) is the widely used catalyst in imine synthesis.[2] Sometimes water absorbents such as molecular sieves,[3] activated alumina[4] and sodium or magnesium sulfate have been used to shift the reaction equilibrium.

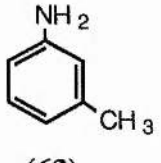
Where R = H or Alkyl or Aryl

Ferrocenecarboxaldehyde **43** obtained as a by-product previously (section 2.1.1.2) was used initially to synthesise ferrocenyl mono- and bis-imines by condensing with aromatic mono- and di-amines in the

presence of PTSA; the water was removed by refluxing with toluene and was separated by using a Dean-Stark assembly, and in some reactions sodium sulfate was also added in the reaction mixture but there was no significant effect of its addition.

4.1.1.1 Reaction of Ferrocenecarboxaldehyde with methyl-aminobenzene.

Ferrocenecarboxaldehyde **43** was condensed with 3-methylamino-benzene **63** in the presence of p-toluenesulfonic acid as a catalyst in refluxing toluene to yield *N*-3-methylbenzeneiminomethylferrocene **64.** The dark brown thick oily product was obtained after the removal of the solvent. The purification of this compound by column chromatography was not possible as the compound starts hydrolysing back to ferrocenecarboxaldehyde on the column. The ^{1}H and ^{13}C NMR of the crude product shows the peaks for ferrocenecarboxaldehyde as well as for the expected aldimine **64.** It was easy to subtract the peaks for the known ferrocenecarboxaldehyde from the NMR spectrum. The ^{1}H NMR spectrum of the product **64** contains a methyl resonance and multiplets integrating to 4 protons in the aromatic region and a characteristic HC=N peak at 8.35 ppm as well as normal monosubstituted ferrocenyl peaks, confirming the intended reaction has taken place. In the ^{13}C NMR spectrum six aromatic peaks, four characteristic peaks for the ferrocenyl group and a peak at 160.1 ppm representative of iminic carbon (HC=N) are present.



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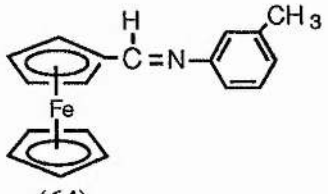
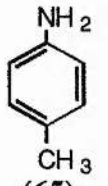
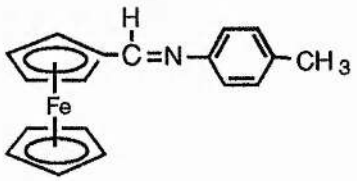


(64)

Another structural isomer of **64**, *N*-4-methylbenzeneiminomethyl-ferrocene **66** was synthesised[5] under similar conditions, by the condensation of ferrocenecarboxaldehyde **43** and 4-methylamino-benzene **65**. The product in this case was isolated as a solid crystalline material by pouring the reaction mixture into chilled diethyl ether after the condensation reaction. The ^{1}H and ^{13}C NMR spectrum are much like those for **64** except that the aromatic region has a doublet of doublets in ^{1}H NMR spectrum in place of the multiplet and only four resonances in the ^{13}C spectrum are observed in contrast to six in **64**, as both the non-quaternary carbons and hence the hydrogens next to the quaternary carbons are chemically and magnetically equivalent.



(65)



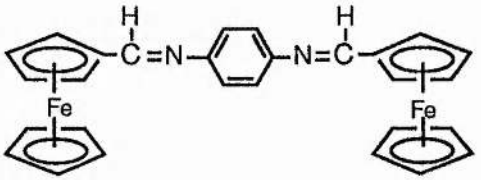
(66)

4.1.1.2 Reaction of Ferrocenecarboxaldehyde with 1,4-diaminobenzene.

A bisferrocenyl bisimine was synthesised by the condensation of two equivalents of ferrocenecarboxaldehyde **43** and one equivalent of 1,4-diaminobenzene **67** in refluxing toluene in the presence of a catalytic amount of *p*-toluenesulfonic acid. The product was precipitated by cooling the reaction mixture in ice after the condensation reaction. The product was characterised as 1,4-benzene-*N,N'*-bis(iminomethyl-ferrocene) **68** by ^{1}H and ^{13}C NMR and elemental analysis. The elemental analysis suggested that the product is a mono-hydrate, and the ^{1}H NMR

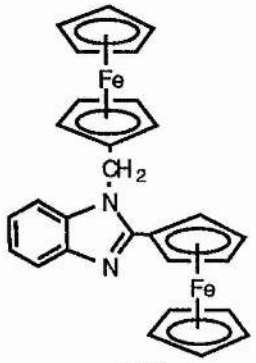
spectrum of the analytical sample also shows a broad peak of water that integrates to one mol H_2O per mol of the compound. The ^1H NMR spectrum also shows a single peak in the aromatic region, as all the four hydrogens on the benzene ring are chemically and magnetically equivalent, along with a characteristic HC=N peak at 8.4 ppm, as well as peaks for monosubstituted ferrocene. The ^{13}C spectrum also shows an iminic resonance at 160.9 ppm along with two peaks in the aromatic region, one quaternary and other non-quaternary, as well as peaks for the ferrocenyl fragments.

(67)

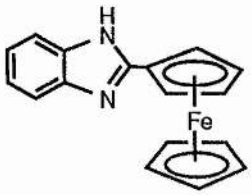


(68)

It is interesting to note here that the attempted reaction between two equivalents of ferrocenecarboxaldehyde **43** and one equivalent of 1,2-diaminobenzene **49** in the presence of *p*-toluenesulfonic acid led to the unexpected synthesis of *N*-ferrocenyl-methyl-2-ferrocenylbenzimidazol **69** and 2-ferrocenylbenzimidazol **70** rather than the intended bisferrocenylbisimine **71**.[6]



(69)



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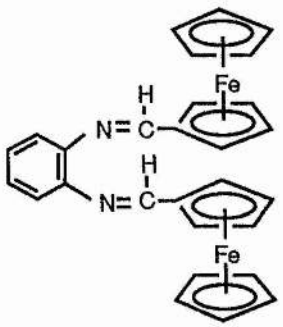


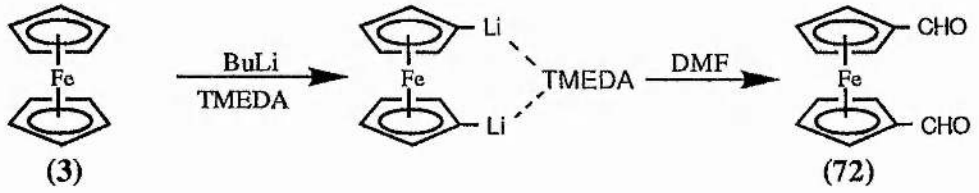
(71)

4.1.2 Ferrocene-containing Polyimines.

Following the reaction in which mono- and bis-imines have been successfully synthesised and characterised, a polycondensation reaction was carried out by using bifunctional-aldehyde, 1,1'-ferrocene-dicarboxaldehyde **72** and bifunctional amine, 1,4-diaminobenzene **67**.

4.1.2.1 1,1'-Ferrocenedicarboxaldehyde .

1,1'-Ferrocenedicarboxaldehyde[7] was synthesised according to published procedure by dilithiation of ferrocene. TMEDA was also used in the reaction mixture to precipitate the dilithio-TMEDA complex to ensure maximum dilithiation of the ferrocene, a reaction that otherwise gives a mixture of ferrocene, monolithioferrocene and dilithioferrocene. The dilithioferrocene-TMEDA precipitate was treated with dry DMF to yield 1,1'-ferrocenedicarboxaldehyde **72** (Equation 4.2). Some ferrocene-carboxaldehyde **43** was also obtained in this reaction. The compound was characterised by ^{1}H and ^{13}C NMR, and the m.p. was also found comparable to the literature value.

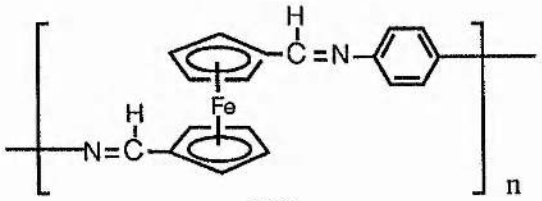


(3) (72) (4.2)

4.1.2.2 Reaction of 1,1'-Ferrocenedicarboxaldehyde with 1,4-diaminobenzene.

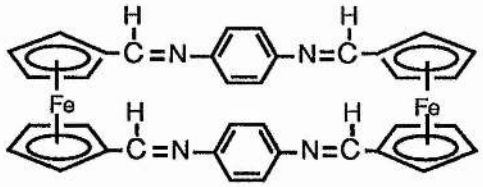
A polycondensation reaction of 1,1'-ferrocenedicarboxaldehyde **72** and 1,4-diaminobenzene **67** under conditions similar to the above

procedures yielded a dark red powder that was precipitated out from the reaction mixture. The precipitated product was found to be insoluble in the common organic solvents; however, it was soluble in concentrated sulfuric acid. The ^1H NMR spectrum in D_2SO_4 has a resonance at 8.85 ppm confirming the identity of the compound as an imine, while another peak at 7.05 represents the aromatic protons and two almost equal-intensity resonances in the ferrocene region represent the 1,1'-disubstituted ferrocene group. The aim of this reaction was to synthesise a polymeric product having a ferrocene fragment in the repeating unit, and a possible structure of the ferrocene-containing polyimine (FCPI) chain is shown in **73**: however there is also a possibility of having the macrocyclic products **74** or **75** as well. The observation that the product in this reaction is insoluble in common organic solvents suggests the presence of some polymeric material, since bisferrocenylbisimine **68** was found to be soluble in dichloromethane although this molecule is bigger than **74** and almost of the same size as **75**. Neither NMR nor elemental analysis helps in any way to differentiate between the two possibilities.



(73)

The attempted use of FAB-mass spectroscopy to gain an estimate of the molecular weight was not successful: most of the peaks were not assignable to any possible fragments of the molecule.



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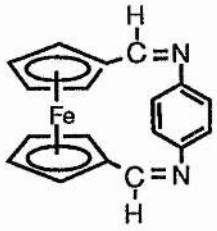

(75)

In order to solve this problem another reaction was carried out in which 20% of the 1,1'-ferrocenedicarboxaldehyde **72** was replaced by the ferrocene monoaldehyde **43** and condensation reaction was carried out with 1,4-diaminobenzene **67** as usual. The dark red product was again precipitated out of the reaction mixture and was again insoluble in common organic solvents. The ^1H NMR spectrum in D_2SO_4 this time showed a small peak due to the unsubstituted Cp ring along with all the previously-observed resonances, revealing that the product is a straight-chain polymer **73** with monosubstituted ferrocene as the end-groups, and not a macrocycle **74** or **75**. The average molecular weight of this polymer is estimated as $2.1x10^3$ from the integration of the unsubstituted and substituted CP rings of the ferrocenes. The calculations of the molecular weight are shown in appendix X. The molecular weight of the polymer that contains no mono substituted ferrocene could not be estimated by the available methods in the laboratory, but it will be a fair assumption that it is higher than $2.1x10^3$ which was the average molecular weight for the polymer that contains 20% ferrocene monoaldehyde in place of ferrocene dialdehyde in the reaction mixture. Another factor that controls the molecular weight of the polymer is the solubility of the product; when the growing chain precipitates out of the reaction mixture, the reaction stops on that chain and hence there is no increase of molecular weight on that chain. The solvent that can hold the growing molecular chain longer in

solution can produce high-molecular weight polymers. No further reactions or investigations for this type of reactions were carried out due to the constraint of time.

4.2 EXPERIMENTAL DETAILS

The NMR spectra were recorded at ambient temperatures, all ^{13}C spectra were recorded as decoupled, in $CDCl_3$ solution unless stated otherwise, on a Bruker AM-300 spectrometer operating at 300.135 MHz for ^{1}H and 75.469 MHz for ^{13}C,. Elemental analysis was carried out in the microanalytical laboratory of the School of Chemistry. Diethylether and light petroleum (b.p. 40-60 °C) were dried over sodium wire, and dichloromethane was distilled over calcium hydride prior to use. DMF was dried over 4 Å molecular sieves and TMEDA was dried and stored over KOH pellets. The aromatic amines were purified according to the published procedures.[8] All the other chemicals were used as received unless stated otherwise.

4.2.1 Synthesis of *N*-3-methylbenzeneiminomethylferrocene.

In a 100 cm^3 3 neck round bottom flask was taken ferrocenecarboxaldehyde **43** (0.3 g, 1.4 mmol), 3-methylaminobenzene **63** (0.13 g, 1.2 mmol), toluene (30 cm^3) and a few crystals of PTSA as a catalyst. The flask was fitted with a condenser having Dean-Stark type assembly. The mixture was refluxed, under nitrogen environment, in an oil-bath for 4 h. After that the mixture was cooled to room temperature. No judgement can be made about the completion of the reaction by using TLC in this case, as the product tends to hydrolyse back by silica gel. The solvent was evaporated and the thick-oily crud-product was

characterised by the NMR spectroscopy. NMR spectrum shows the peaks for unreacted ferrocenecarboxaldehyde as well as *N*-3-methylbenzeneiminomethyl-ferrocene **64**.

For *N*-3-methylbenzeneiminomethylferrocene **64**;

δH($CDCl_3$) 2.4 (s, 3H, CH_3), 4.25 (s, 5H, C_5H_5), 4.48 (t, 2H, C_5H_4), 4.80 (t, 2H, C_5H_4), 6.95-7.28 (m, 4H, C_6H_4), 8.45 (s, 1H, -HCN-).

δC($CDCl_3$) 21.4 (s, 1C, CH_3), 69.0 (s, 2C, C_5H_4), 69.2 (s, 5C, C_5H_5), 71.3 (s, 2C, C_5H_4), 80.3 (s, 1C, ipso-C_5H_4), [117.5, 121.3, 125.9 and 128.9] (s, 1C, C_6H_4), [138.8 and 152.5] (s, 1C, ipso-C_6H_4), 161.0 (s, 1C, -HCN-).

For ferrocenecarboxaldehyde **43**:

δ_H($CDCl_3$) 4.30 (5H, s, C_5H_5), 4.60 (2H, C_5H_4), 4.80 (2H, C_5H_4) and 9.95 (1H, s, CHO).

δ_C($CDCl_3$) 69.6 (5C, s, C_5H_5), 73.1(4C, s, C_5H_4), 79.3 (1C, s, *ipso*-C_5H_4) and 193.3 (1C, s, CHO).

4.2.2 Synthesis of *N*-4-methylbenzeneiminomethylferrocene.[5]

In a 100 cm^3 3 neck round bottom flask was taken ferrocenecarboxaldehyde **43** (0.22 g, 1.0 mmol), 4-methylaminobenzene **65** (0.15 g, 1.4 mmol), toluene (30 cm^3) and a few crystals of PTSA as a catalyst. The flask was fitted with a condenser having Dean-Stark type assembly. The mixture was refluxed, under nitrogen environment, in an oil-bath for 4 h, the volume of the reaction mixture was reduced to minimum and was poured in chilled diethylether. *N*-4-methylbenzene-iminomethylferrocene **66** precipitated out as a brown-red crystalline material (0.22g, 84.9%). The precipitate was washed with cold diethyl-

ether to remove any unreacted starting material. Identity of the compound was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

$\delta H(CD_2Cl_2)$ 2.45 (s, 3H, CH_3), 4.25 (s, 5H, C_5H_5), 4.50 (s, 2H, C_5H_4), 4.95 (t, 2H, C_5H_4), 6.95-7.35 (m, 4H, C_6H_4), 8.45 (s, 1H, -HCN-).
$\delta C(CD_2Cl_2)$ 21.5 (s, 1C, CH_3), 69.7 (s, 2C, C_5H_4), 70.0 (s, 5C, C_5H_5), 71.9 (s, 2C, C_5H_4), 81.6 (s, 1C, ipso-C_5H_4), [121.2 and 130.4] (s, 2C, C_6H_4), [135.5 and 151.0] (s, 1C, ipso-C_6H_4), 160.8 (s, 1C, -HCN-).

4.2.3 Synthesis of 1,4-Benzene-*N,N'*-bis(iminomethyl-ferrocene).

In a 100 cm^3 3 neck round bottom flask was taken ferrocenecarboxaldehyde **43** (0.22 g, 1.0 mmol), 1,4-diaminobenzene **67** (0.06 g, 0.05 mmol), toluene (30 cm^3) and a few crystals of PTSA as a catalyst. The flask was fitted with a condenser having Dean-Stark type assembly. The mixture was refluxed, under nitrogen environment, in an oil-bath for 4 h, and then was cooled in an ice bath. 1,4-Benzene-*N,N'*-bis(iminomethylferrocene) **68** precipitated out as a shiny-brown crystalline solid (0.11g, 44%) that was washed with diethylether and methylcyclohexane to remove any unreacted starting material. The volume of the filtrate was reduced to minimum and was poured in chilled diethylether that yielded the second crop of the product **68** (0.11g, *ca.* 44%). The NMR of the second crop suggested that it is contaminated with *ca.* 20% monoimine product, a bit longer reaction time may have helped to convert all to the required bisimine. The compound **68** was characterised by ^{1}H and ^{13}C NMR spectroscopy and by elemental analysis. The elemental analysis suggested the nature of the bis-imine

product **68** as a mono-hydrate, ^1H NMR spectrum also shows a broad water peak integrating to one mole H_2O per mole of the product.

Anal. found C 65.2%, H 4.7%, N 5.1%; $C_{28}H_{24}FeN_2$ requires C 67.2%, H 4.8%, N 5.6%; $C_{28}H_{24}FeN_2.H_2O$ requires C, 65.4%; H, 5.0%; N, 5.4%.

$\delta H(CD_2Cl_2)$ 4.25 (s, 5H, 2 x C_5H_5), 4.50 (s, 2H, 2 x C_5H_4), 4.80 (t, 2H, 2 x C_5H_4), 7.15 (s, 4H, C_6H_4), 8.40 (s, 1H, 2 x HCN).

$\delta C(CD_2Cl_2)$ 69.7 (s, 2C, 2 x C_5H_4), 70.0 (s, 5C, 2 x C_5H_5), 72.0 (s, 2C, C_5H_4), 81.5 (s, 1C, 2 x *ipso*-C_5H_4), 122.1 (s, 4C, C_6H_4), 150.8 (s, 2C, 2 x *ipso*-C_6H_4), 160.9 (s, 1C, 2 x HCN).

4.2.4 Synthesis of 1,1'-Ferrocenedicarboxaldehyde.[7]

In a nitrogen-flushed three-neck 250 cm^3 flask equipped with stirrer and reflux condenser, ferrocene (4.0 g, 0.022 mol) was dissolved in dry petroleum ether 40/60 (100 cm^3) and tetramethylethylenediamine (TMEDA) (8 cm^3, 0.053 mol) was added. The mixture was stirred while 1.6 M ^{n}BuLi (30 cm^3, 0.058 mol) was transferred drop-wise under positive pressure of nitrogen. This produced a homogeneous solution that was stirred overnight under nitrogen at room temperature. An orange precipitate formed during this period, the stirring was stopped and the supernatant solution containing unreacted TMEDA, ^{n}BuLi and ferrocene was removed through a cannula under positive pressure of nitrogen. Fresh dry petroleum ether (100 cm^3) was added and was drained after some stirring as above.

Dry petroleum ether 40/60 (100 cm^3) was added again to the orange precipitate and dry DMF (3.6 cm^3) was added drop-wise in the stirred

suspension. After 30 min of stirring 15% HCl (60 cm^3) was added to this solution. The addition of HCl produced a red solid that was precipitated out, that was filtered and washed with petroleum ether. The aqueous layer was extracted in dichloromethane. The combined product was purified on a silica gel column giving 1,1'-ferrocenedicarboxaldehyde **72** (4.15g, 79.8%) as a red solid and ferrocenecarboxaldehyde **43** (0.5g, ca. 10%) as orange red solid, confirmed by TLC compared to an authentic sample.

For 1,1'-ferrocenedicarboxaldehyde **72.**
m.p. 179-180.5 °C (lit. 179-180 °C)[7]
δH($CDCl_3$) 4.60 (s, 2H, 2 x C_5H_4), 4.80 (s, 2H, 2 x C_5H_4), 9.85 (s, 1H, 2 x CHO).
δC($CDCl_3$) 70.5 (s, 2C, 2 x C_5H_4), 73.9 (s, 2C, 2 x C_5H_4), 79.9 (s, 1C, 2 x *ipso*-C_5H_4), 192.6 (s, 1C, 2 x CHO).

4.2.5 Synthesis of Ferrocene-containing polyimines.

a. Using ferrocenedicarboxaldehyde.

In a 100 cm^3 3 neck round bottom flask was taken 1,1'-ferrocenedicarboxaldehyde **72** (0.25 g, 1.0 mmol), 1,4-diaminobenzene **67** (0.11 g, 1.0 mmol), toluene (50 cm^3) and a few crystals of PTSA as a catalyst. The flask was fitted with a condenser having Dean-Stark type assembly. The mixture was refluxed, under nitrogen environment, in an oil-bath for 4 h during that time dark-red solid precipitated out of the reaction mixture. The precipitated material (0.3 g) was filtered and washed with toluene to remove any unreacted starting material. This solid powder was insoluble in common organic solvents but was soluble in concentrated sulfuric acid; the change of ferrocene to ferrocenium is

visible from the change of red to green colour in sulfuric acid. A ^1H NMR study of the D_2SO_4 solution confirms the identity of the product as ferrocene-containing imine, but there is no clue that the product here is a polymer **73** or a macrocycle **74** or **75**.

$\delta H(D_2SO_4)$ 4.92 (s, 2H, C_5H_4), 5.27 (s, 2H, C_5H_4), 7.05 (s, 4H, C_6H_4), 8.82 (s, 1H, -HCN-).

b. Using a mixture of ferrocenealdehyde and ferrocenedialdehyde.

The procedure and work-up was same as above. The composition of the reaction mixture was 1,1'-ferrocenedicarboxaldehyde **72** (0.20 g, 0.8 mmol), ferrocenecarboxaldehyde **43** (0.09, 0.4 mmol), 1,4-diamino-benzene **67** (0.11 g, 1.0 mmol), toluene (50 cm^3) and a few crystals of PTSA as a catalyst. The product obtained was same as above and was not soluble in common organic solvents. A ^1H NMR spectrum in D_2SO_4 shows all the above peaks in addition to a peak representing unsubstituted *Cp* ring from the end-group ferrocenyl moieties. This confirms the open chain polymerisation reaction rather than macrocyclic reaction. The average molecular weight of this ferrocene-containing polyimine (FCPI) polymer is calculated *ca.* $2.1x10^3$ (Appendix X).

$\delta H(D_2SO_4)$ 4.82 (s, 5H, C_5H_5) 4.95 (s, 2H, C_5H_4), 5.25 (s, 2H, C_5H_4), 7.05 (s, 4H, C_6H_4), 8.82 (s, 1H, -HCN-).

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CHAPTER 5

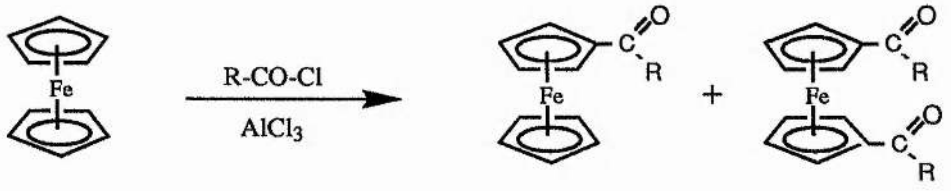
Ferrocene-Containing Ketones

In this chapter Friedel Crafts acylation reactions to produce ferrocenyl ketones are described. Employment of diacylating agents, such as biphenyldicarbonylchloride and benzenedicarbonylchloride, in this reaction has produced diferrocenyl-diketone compounds. As ferrocene itself can act as a bifunctional substrate in Friedel Crafts reactions, the use of diacylating agents with ferrocene has been investigated to produce polyketones (PKs) that have ferrocene moieties in the main chain of the polymers. An estimate of the average molecular weight of the resulting polymers has also been made.

5.1 RESULTS AND DISCUSSION

5.1.1 Friedel Crafts acylation reactions of ferrocene.

The Friedel Crafts acylation reaction of ferrocene, producing acylferrocenes or ferrocenyl monoketones has been known[1] almost since the discovery of ferrocene[2] itself. In this type of reaction ferrocene is reacted with an acyl chloride in the presence of a Lewis acid such as $AlCl_3$ or $FeCl_3$ (Equation 5.1). Ferrocene can undergo homoannular mono-acylation or heteroannular bis-acylation. In this thesis Friedel Crafts acylation reaction has already been exploited to synthesise the homoannular acyl ferrocene **41** (section 2.2.1.1.8) and the heteroannular bisacyl ferrocene **47** (section 2.2.2.3). Now the use of bifunctional aromatic diacylating agents with ferrocene is reported.

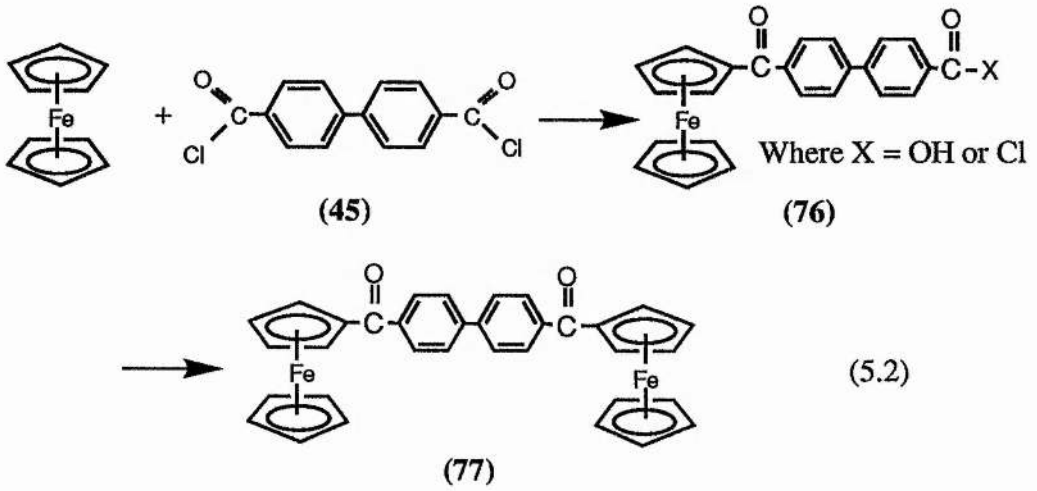


(5.1)

5.1.1.1 Reaction of ferrocene and biphenyldicarbonylchloride.

When 4,4'-biphenyldicarbonylchloride **45** was reacted with more than two-fold excess of ferrocene **3** under Friedel Crafts condition in the presence of $AlCl_3$ to yield 4,4'-biphenyl-bis(ferrocenylketone) **77**, the reaction proceeded smoothly and the TLC of the reaction mixture showed, in the early stages of the reaction, a less-polar red spot that almost vanished by the end of the reaction and a new more-polar red spot appeared corresponding to **77**. The less-polar spot corresponds to the mono-acylation of a single ferrocene molecule by 4,4'-biphenyl-

dicarbonylchloride (see below). The compound **77** was isolated by chromatography and was readily characterised by ^{1}H and ^{13}C NMR and elemental analysis.



(45) (76) (77) (5.2)

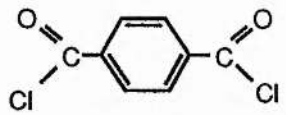
The ^{1}H NMR spectrum of the compound **77** shows peaks characteristic of a mono-substituted ferrocene with relative intensities of 5:2:2 and two doublets of equal intensities in the aromatic region, corresponding to the biphenyl protons. The ^{13}C NMR spectrum shows a ketonic resonance at 198.5 ppm, four peaks in the aromatic region along with four peaks in the ferrocene region, including one for quaternary carbon, one for the unsubstituted Cp ring and two arising from the two sets of magnetically equivalent carbons in the substituted Cp ring. The ^{1}H NMR spectrum also shows a broad peak for the water integrating to about one mol of water per mol of the compound. When elemental analysis was compared with that calculated for the monohydrate, it was found satisfactory. Successive attempts to grow crystals of compound **77** for single crystal X-ray analysis yielded very small crystals that grow in conglomerates which were always unsuitable for single crystal X-ray crystallography.

In order to identify the reaction intermediate **76** that is presumably the result of the single acylation of ferrocene at one end of acid chloride in **45**, another reaction was carried out under similar conditions, with equimolar quantities of ferrocene **3** and 4,4'-biphenyldicarbonylchloride **45**. It was observed by TLC that in the beginning monoacylation product **76** was formed, as expected, but then diacyl product **77** also started forming and with time the abundance of the intermediate started decreasing. By constantly monitoring the progress of the reaction by TLC it is possible to quench this reaction when the abundance of the intermediate **76** is at its maximum. Chromatography on silica gel yielded a small fraction of the intermediate, enough for characterisation purposes. In the ^{1}H NMR spectrum the ferrocenyl fragment showed its usual resonances while four doublets of equal intensities were observed in the aromatic region representing the four pairs of protons on biphenyl group; in the ^{13}C spectrum, besides the ferrocenyl resonances there were eight resonances, of which four were quaternary, observed in the aromatic region along with the two carbonyl peaks, one at 198.4 ppm characteristic of a ketonic group and the other at 168.0 ppm corresponding to an acid or an acid chloride. Hence the compound **76** could be an acid or an acid chloride and NMR studies cannot differentiate between the two possibilities, because acidic COOH sometimes does not appear in ^{1}H spectrum and the position for carboxylic (-COOH) and acid chloride (-COCl) carbon lies in the same region of the ^{13}C spectrum; however it can be surmised that the product is an acid chloride on the basis of the initial observation that this compound was found less polar on TLC. Attempts to grow crystals from dichloromethane-diethylether mixture yielded a few very thin plate-like crystals of the compound **76** which

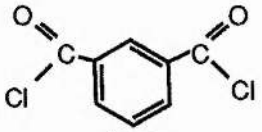
were immediately sent for the X-ray analysis. The results of the single crystal X-ray analysis confirmed the identity of the product **76** as an acid chloride, despite the chance of hydrolysis of the -C(O)Cl bond during the work-up or during chromatography. Figure 5.1 shows the single crystal X-ray structure of 4-ferrocenylketone-4'-biphenylcarbonylchloride **76**. The discussion on the crystal and molecular structure of this compound is given in section 5.1.2.

5.1.1.2 Reaction of ferrocene and benzenedicarbonylchlorides.

Following the reactions of biphenyldicarbonylchloride with ferrocene some more Friedel Crafts acylation reactions were carried out employing 1,4-benzenedicarbonylchloride **78** (terephthaloyl chloride) and 1,3-benzenedicarbonylchloride **79** (isophthaloyl chloride) as the diacylating agent.



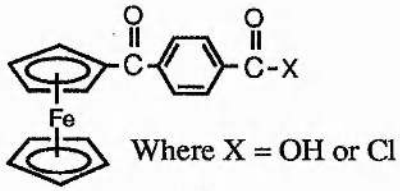
(78)



(79)

The reaction of 1,4-benzenedicarbonylchloride **78** with excess of ferrocene did not proceed after the first acylation even under reflux for 24 h in dichloromethane, and attempts to carry out this reaction, under reflux, in other high boiling solvents such as 1,1,1-trichloroethane and nitrobenzene were also not promising: reaction in 1,1,1-trichloroethane showed on TLC, a small amount of mono-acyl product with a lot of tar and in nitrobenzene no reaction at all was obseved. The monoacylated ferrocene **80** was isolated in modest yield from the reaction mixture, using dichloromethane as a solvent, and was characterised by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of this compound shows the

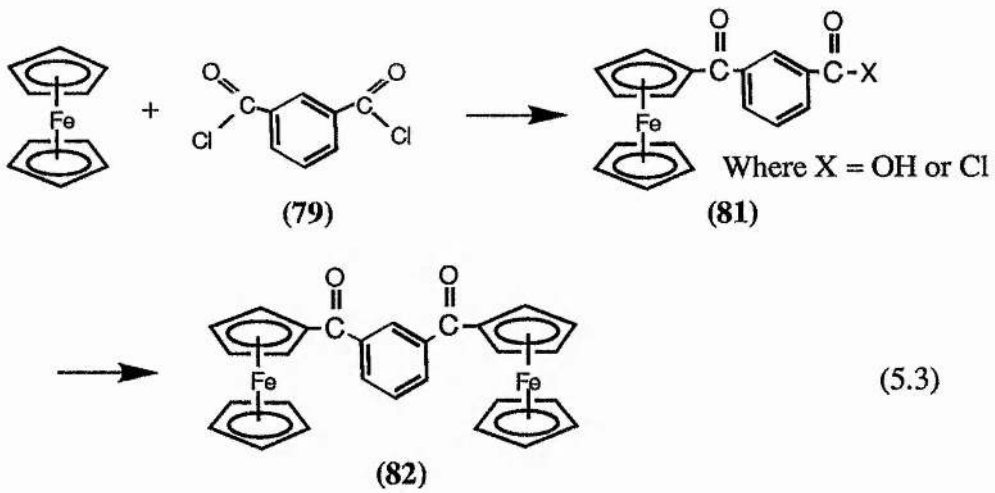
peaks characteristic of the mono-substituted ferrocene and two doublets of almost equal intensity in the aromatic region. The ^{13}C spectrum also shows the usual resonances of the mono-substituted ferrocene as well as four aromatic and two carbonyl peaks; one of them, at 198.1 ppm represents a ketonic group and the other at 167.9 ppm represents a carboxylic acid or an acid chloride, similar to compound **76** that has the carbonyl resonances at 198.4 and 168.0 ppm respectively and was characterised by single-crystal X-ray analysis. Based on the findings in the case of compound **76** and consistent with the previous observation that mono-acylated product is less polar and that the R_f of compounds **76** and **80** are comparable, it is assumed that the compound **80** is 1-carbonylchloride-4-ferrocenylketonebenzene.



Where X = OH or Cl

(80)

In the case of the reaction of 1,3-benzenedicarbonylchloride **79** and excess ferrocene the reaction proceeded well (Equation 5.3). The reaction sequence was the same as previously observed and in the beginning of the reaction mono-ferrocenylketone **81** was formed that gradually disappeared and the diacyl diferrocenyl compound **82** was the final product. The diacyl diferrocenyl product, 1,3-benzene-bis-(ferrocenylketone) **82** was isolated in good yield and characterised by NMR and elemental analysis. The intermediate **81** was also isolated by quenching a similar reaction when its abundance was estimated maximum by TLC experiment.



(5.3)

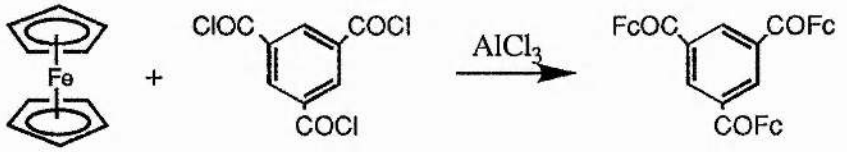
The ^{1}H NMR spectrum of compound **82** consists of a triplet, two doublets and a singlet in the aromatic region alongwith the usual ferrocenyl resonances, the ^{13}C NMR spectrum also shows four peaks in the aromatic region indicating four non-equivalent groups of carbons in the aromatic region in addition to a ketonic resonance at 198.5 ppm and normal ferrocenyl resonances except the quaternary carbon that is perhaps overlapping with the solvent's peaks. The ^{1}H NMR spectrum of the compound **81** consists of four peaks in the aromatic region and the characteristic pattern of mono-substituted ferrocene resonances. The ^{13}C NMR spectrum exhibited six carbons in the aromatic region, as all the six carbons are non-equivalent, along with two carbonyl resonances one ketonic resonance at 197.4 ppm and another at 168.0 ppm for acid chloride; similar to **76**, that was characterised by single-crystal X-ray differection studies, and has the carbonyl resonances at 198.4 and 168.0 ppm. On the basis of the findings for compound **76** and because compound **81** is mobile on TLC and the R_f is matching with that of **76**, it is assumed that the compound **81** is also an acid chloride.

The comparison of the acylation reactions of dicarbonyl chlorides **78**, **79** and **45** show that as in **79** the two carbonyl chlorides are *meta* to each other they are not affected by each other through mesomeric effect and the fastest reaction occur there. In compound **78** the two acyl groups are *para* to each other hence one acyl group may affect the other through the ring conjugation and hence after one acylation the reaction does not proceed for the second acylation. In the case of purely organic compounds Olah[3] has reported the formation of diacyl compounds but has said that there is not enough data available to make a comparison. While in compound **45** the two acyl groups are on two different phenyl groups that are joined by a single bond and the free rotation along the single bond may restrict the communication between the two acyl groups and both the acyl groups behave independently, resulting the formation of bis(ferrocenyl ketone) **77**.

5.1.1.3 Reaction of ferrocene and benzenetricarbonylchloride.

Another reaction was carried out, under similar conditions, between ferrocene and 1,3,5-benzenetricarbonylchloride **83**, having in mind the potential use of the compound **83** as a cross-linking agent in the intended polymerization reactions between ferrocene and bisacylchlorides. The reaction was found very slow in refluxing dichloromethane, and the examination of the TLC of the reaction mixture showed the presence of expected mono- di- and tri-acyl mono-, bis-, and tris-ferrocenes. No attempts were made to stop the already sluggish reaction to extract the reaction intermediates. The reflux in dichloromethane for 24 h rendered 1,3,5-benzene-tris(ferrocenylketone) **84** in low yield (Equation 5.4), and most of the unreacted ferrocene was recovered. The compound **84** was

characterised by its very simple NMR spectrum. containing just one peak in the aromatic region with the usual ferrocenyl peaks in the ^{1}H spectrum and in the ^{13}C spectrum, together with two peaks arising from the quaternary and non-quaternary carbons of substituted benzene, and one representing the ketonic carbon.



(3) (83) (84) (5.4)

5.1.2 Crystal and molecular structure of compound 76.

4-Ferrocenylketone-4'-biphenylcarbonylchloride **76** was crystallized from the solution in dichloromethane-diethyl ether by slow evaporation at room temprature and the crystal suitable for single crystal X-ray diffraction analysis were studied.

The systematic absences permitted two possible space groups, Cc and C2/c. The unit-cell dimensions, together with an estimated density of *ca.* 1.4 - 1.5 g cm^{-3} typical of the densities found in other acyl ferrocenes, indicated Z = 16, i.e. Z' = 4 for Cc or Z' = 2 for C2/c. However, attempts to solve the structure, either by direct methods or by Patterson methods, were uniformly unsuccessful in both of the possible space groups. Careful inspection of the intensity statistics at this point revealed that the population of the parity groups *eee* and *eeo* was far higher than that of the groups *ooe* and *ooo*, while the other four groups were systematically absent. This intensity distribution suggested an alternative approach to the structure solution.

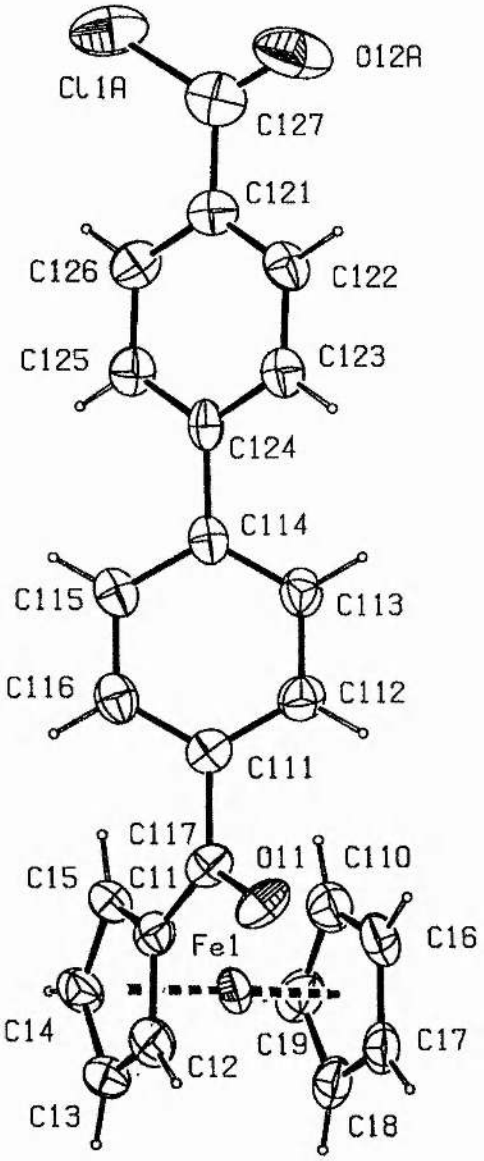


Figure 5.1 Single crystal X-ray structure of 4-ferrocenylketone-4'-biphenylcarbonylchloride ***76****; view of one of the four molecules in the space group Cc with atomic numbering scheme.*

Use of only the *eee* and *eeo* data, and conversion to a quarter-sized unit cell (**a** –> **a**/2; **b** –> **b**/2; **c** –> **c**) with an appropriate origin shift allowed a straightforward Patterson solution in $P2_1/c$ with $Z' = 1$. Development of this solution revealed all the carbon atoms of the ferrocenyl fragment with full occupancy, and two $COC_6H_4C_6H_4COCl$ fragments, one bonded to each cyclopentadienyl ring and each having site occupation factor 0.5. Refinement of this disordered $P2_1/c$ solution using only the *eee* and *eeo* groups of the original data, suitably transformed, converged at R = 0.05.

Conversion of the $P2_1/c$ solution back to the original cell and testing the various possibilities for the location of the $COC_6H_4C_6H_4COCl$ groups confirmed the space group as Cc. Refinement, with the aryl and cyclopentadienyl rings modelled as planar regular pentagons and hexagons respectively, was possible only in Cc. No solution or refinement was feasible in C2/c. At this point it was clear that the four independent iron atoms in Cc generated an almost exact $P2_1/c$ pattern of coordinates in the quartered cell. Because of the correlation introduced into the refinement by this pseudo-symmetry, and because of the large number of parameters required for full anisotropic refinement, the subsequent refinement in Cc was carried out with the application of heavy restraints on the values of the displacement parameters.

The asymmetric unit of compound **76** consists of four independent molecules: in three of these molecules, those containing Fe1, Fe3 and Fe4, the terminal carbonylchloride group is disordered with two orientations of this fragment differing by a 180° rotation about the exocyclic C(aryl)-C(O)Cl bond. For the three molecules disordered in

this manner, the two orientations are in the ratios 0.51(1):0.49(1), 0.70(1):0.30(1) and 0.56(1):0.44(1) respectively.

As is often observed in systems where there is an excess of hard hydrogen-bond acceptors, in this case the ketonic oxygen atoms, there are C-H···O hydrogen bonds with aryl carbon atoms acting as the donors. The pairwise development of such interactions serves to link pairs of molecules into cyclic dimers. Carbon atom C123 in molecule 1 at (x, y, z) acts as donor towards the ketonic oxygen O31 in molecule 3 at (0.5 + x, 0.5 - y, 0.5 + z), while C323 in molecule at (0.5 + x, 0.5 - y, 0.5 + z) in turn acts as donor to O11 in molecule 1 at (x, y, z), so generating a dimeric motif characterised by an $R_2^2(18)$ ring.[4] Similarly molecule 2 at (x, y, z) and molecule 4 at (0.5 + x, 1.5 - y, 0.5 + z) are linked by a pair of C-H···O hydrogen bonds into a second $R_2^2(18)$ motif. These four independent C-H···O hydrogen bonds all have d(H···O) (un-normalised) < 2.50 Å, d(C···O) < 3.40 Å, and <(C-H···O) > 160°. Hence all should be regarded as strong examples of their type.[5] The two independent $R_2^2(18)$ rings are both approximately centrosymmetric around the points (0.5, 0.125, 0.5) and (0.5, 0.625, 0.5) respectively: in the $P2_1/c$ solution, these rings would be precisely centrosymmetric.

5.1.3 Polymerisation reactions of ferrocene and aromatic dicarbonylchlorides.

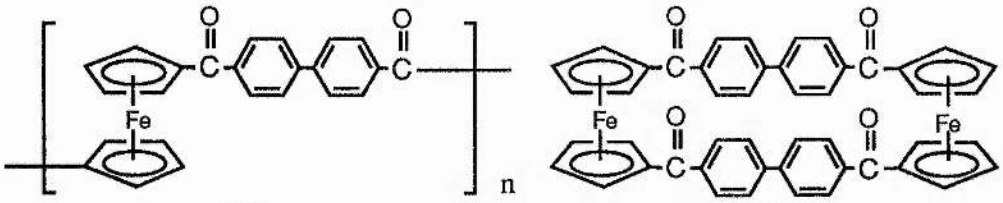
It is known that under Friedel Crafts conditions ferrocene can undergo heteroannular bis-acylation[6] i.e. can act as a bifunctional monomer in Friedel Crafts acylation reactions. Following the observation that both the carbonyl chlorides in 4,4'-biphenyldicarbonylchloride **45**

and 1,3-benzenedicarbonylchloride **79** can act as a bifunctional acylating agents, polymerization reactions were carried out by using exactly equi-molar quantities of ferrocene **3** and aromatic dicarbonylchlorides **45** and **79**.

5.1.3.1 Polymerization reaction of ferrocene and 4,4'-biphenyldicarbonylchloride.

When 4,4'-biphenyldicarbonylchloride **45** was reacted with ferrocene **3** under Friedel Crafts conditions, after 48 h stirring at 30 °C some red insoluble product precipitated out that is most plausibly the ferrocene-containing polyketone (FCPK) polymer. TLC of the reaction mixture showed the presence of the intermediate, 4,4'-biphenyl-bis(ferrocenyl-ketone) **77**, so the mixture was further refluxed for 4 h to ensure the completion of the reaction. The precipitated product was not very soluble in common organic solvents but was sparingly soluble in $CDCl_3$. The ^1H NMR spectrum shows a peak of the unsubstituted Cp ring in mono-substituted ferrocene besides two peaks of equal intensity arising from the substituted Cp ring, which shows that ferrocene is the end group in the polymer chain, which is apparent because it is known[7] that the presence of an acyl group on one of the Cp rings in ferrocene reduces the rate of heteroannular second acylation by a factor of *ca.* $2x10^4$. The ratio of the substituted to unsubstituted Cp rings gives an estimate of the average molecular weight of the polymer. The average molecular weight calculated on the basis of the ^1H NMR integration is $1.75x10^3$ (Appendix XII). The repeating unit of the ferrocene-containing polyketone (FCPK) is shown in structure **85**. The other possibility of the reaction of the

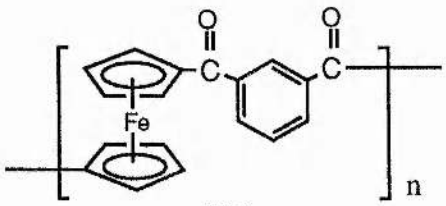
formation of a macrocycle **86** can easily be ruled out on the basis of the presence of the unsubstituted Cp ring in ^{1}H NMR spectrum.



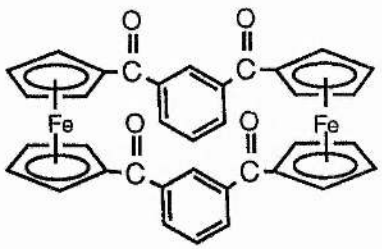
(85) **(86)**

5.1.3.2 Polymerization reaction of ferrocene and 1,3-benzenedicarbonylchloride.

When a polymerization reaction was carried out using 1,3-benzenedicarbonylchloride **79** and ferrocene **3** as the monomers, under Friedel Crafts conditions in dichloromethane, a dark-red solid was precipitated that was characterised as ferrocene-containing polyketone (FCPK) polymer **87**. The product **87** was also accompanied by another soluble product that was precipitated as a red-powder by adding light petroleum ether. There were two possibilities for the nature of this product either, a low molecular weight polymer or a macrocycle **88** or **89**.



(87)



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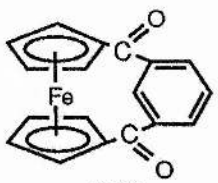

(89)

The initially precipitated polymer **87** was soluble to some extent (more than the polymer **85**) in $CDCl_3$ and the ^1H NMR spectrum in the ferrocene region shows two large resonances of equal intensities, corresponding to the substituted Cp ring, and a relatively small peak corresponding to the unsubstituted Cp ring. The aromatic region shows three peaks, corresponding to the protons on the 1,3-disubstituted benzene. The ratio of the peaks of the substituted to unsubstituted Cp rings in the ferrocene region gives an estimation of the average molecular weight of the polymer *ca.* 1.04×10^4 (Appendix XIII). The FTIR spectrum of the polymer **87** shows a strong ketonic absorption at 1644 cm^{-1}.

The NMR studies of the soluble fraction of the product, that was precipitated by adding light petroleum, show no peaks corresponding to the unsubstituted Cp ring in either ^1H or ^{13}C spectrum. Two possibilities arises from this observation; first is that the product has an infinite chain length, if that was so it should have precipitated with the other polymeric material, the second and most plausible possibility is that the compound is a macrocycle such as **88** or **89** so there is no mono substituted ferrocene and hence no unsubstituted Cp ring.

The attempts to get an estimate of the average molecular weights of the polymer **87** or macrocycle **88** or **89** by FAB-mass spectrometry were not fruitful and most of the peaks listed were not assignable to the apparently possible fragments of the compounds.

5.2 EXPERIMENTAL DETAILS

The NMR spectra were recorded at ambient temperatures, all ^{13}C spectra were recorded as decoupled, in $CDCl_3$ solution unless stated otherwise, on a Bruker AM-300 spectrometer operating at 300.135 MHz for ^{1}H and 75.469 MHz for ^{13}C . Elemental analysis was carried out in the microanalytical laboratory of the School of Chemistry. Diethylether and light petroleum (b.p. 40-60 °C) were dried over sodium wire, and dichloromethane was distilled over calcium hydride prior to use. All the other chemicals were used as received unless stated otherwise.

5.2.1 Synthesis of 4,4'-biphenylbis(ferrocenylketone).

In a 500 cm^3 three neck round bottom flask fitted with a condenser, biphenyldicarbonylchloride (5.58 g, 20 mmol) and anhydrous aluminium chloride (6.0 g, 45 mmol) were stirred under nitrogen in dry dichloromethane (100 cm^3) and ferrocene (4.1 g, 22 mmol) in dry dichloromethane (100 cm^3) was added dropwise. The colour of the solution changed to dark blue on addition of ferrocene and an exothermic reaction occurred as the dichloromethane was observed condensing on the walls of the flask and the condenser, the evolution of the HCl gas was also noticed by change in colour of blue litmus. The reaction was followed by TLC; in the beginning one less polar spot and another relatively more polar spot were observed, the less polar spot almost disappeared with time. The reaction mixture was stirred for 24 h at 30 °C and than was refluxed for 2 h to ensure the completion of the reaction. The reaction mixture was poured onto ice water mixture and product was extracted in dichloromethane. The dichloromethane extract was washed

with dilute HCl followed by distilled water to completely remove $AlCl_3$ from the product. The organic phase was dried (Na_2SO_4), concentrated and chromatographed over silica gel using dichloromethane as mobile phase to produce 4,4'-biphenylbis(ferrocenylketone) **77** (9.2 g, 80%) as a red solid.

Anal. found C 68.7%; H 4.5%; $C_{34}H_{26}Fe_2O_2.H_2O$ requires C 68.5%; H 4.7%; $C_{34}H_{26}Fe_2O_2$ requires C 70.6%; H 4.5%.

$\delta_H(CDCl_3)$ 4.27 (s, 10H, 2 x C_5H_5), [4.62 and 5.0 (t, 4H, 2 x C_5H_4)], 7.76 and 8.04 (d, 8H, 2 x C_6H_4).

$\delta_C(CDCl_3)$ 70.3 (s, 2 x C_5H_5); 71.5 and 72.7 (s, 2 x C_5H_4), 78.2 (s, *ipso*-2 x C_5H_4), 127.0 (s), 128.8 (s), 139.1 (s) and 143.2 (s) (s, 2 x C_6H_4); 198.6 (s, 2 x CO).

5.2.2 Synthesis of 4-ferrocenylketone-4'-biphenyl-carbonylchloride.

In order to confirm the reaction intermediate in the above reaction, biphenyldicarbonylchloride (0.61 g, 2.0 mmol) was added in small portions to a well-stirred solution of ferrocene (0.37 g, 2.0 mmol) and anhydrous $AlCl_3$ (0.30 g, 2.2 mmol) in dry CH_2Cl_2 (150 cm^3) at 0 °C. The reaction was monitored by TLC; when it was judged that the abundance of the less-polar product was at a maximum, the reaction mixture was quenched by filtering the reaction mixture onto ice. The organic product was extracted into CH_2Cl_2, and this fraction was washed with water until the washings were neutral. The extract was dried and concentrated, and then chromatographed on silica with 10% petroleum in CH_2Cl_2 as eluent to give 4-ferrocenylketone-4'-biphenylcarbonylchloride **76** enough for the characterisation purpose.

$\delta_H(CDCl_3)$ 4.26 (s, 5H, C_5H_5), 4.67 (t, 2H) and 4.98 (t, 2H) (C_5H_4), 7.72, 7.82, 8.05 and 8.28 (d, 2H, biPh).

$\delta_C(CDCl_3)$ 70.4 (s, C_5H_5); 71.6 (s), 72.9 (s) and 78.1 (s, *ipso*) (C_5H_4), [127.3, 127.7, 128.9 and 132.1 (s, biPh)], [132.4, 139.8, 142.0 and 147.0 (s, biPh, ipso)], 168.0 (s, COCl); 198.4 (s, COFc).

5.2.3 Synthesis of 1-carbonylchloride-4-ferrocenyl-ketonebenzene.

In a 250 cm^3 three neck round bottom flask fitted with a condenser, 1,4-benzenedicarbonylchloride (1.0 g, 5 mmol) and anhydrous aluminium chloride (2.0 g, 15 mmol) were stirred under nitrogen in dry dichloromethane (50 cm^3) and ferrocene (1.86 g, 10 mmol) in dry dichloromethane (50 cm^3) was added dropwise. The colour of the solution changed to dark blue on the addition of ferrocene and evolution of HCl gas was observed by blue litmus paper. The reaction was observed by TLC; after the appearance of the first less polar spot, reaction did not proceed further and no spot corresponding to diferrocenyl compound was observed even after reflux for 24 h. The reaction mixture was poured onto ice water mixture and product was extracted in dichloromethane. The dichloromethane extract was washed with dilute HCl followed by distilled water to completely remove $AlCl_3$ from the product. The organic phase was dried (Na_2SO_4), concentrated and chromatographed over silica gel using petrol:dichloromethane (1:10) as mobile phase to produce 1-carbonylchloride-4-ferrocenylketone-benzene **80** (0.35 g, 20%) as a red crystalline solid.

$\delta_H(CDCl_3)$ 4.25 (s, 5H, C_5H_5), 4.68 (t, 2H) and 4.90 (t, 2H) (C_5H_4), 7.98 and 8.24 (d, 2H, C_6H_4).

$\delta_C(CDCl_3)$ 70.4 (s, C_5H_5); 71.4 (s), 73.4 (s) and 77.2 (s, *ipso*) (C_5H_4), [128.2 and 131.3 (s, C_6H_4)], [135.1 and 145.4 (s, C_6H_4, *ipso*)], 167.9 (s, COCl); 198.1 (s, COFc).

5.2.4 Synthesis of 1,3-benzenebis(ferrocenylketone).

In a 100 cm^3 three neck round bottom flask fitted with a condenser, 1,3-benzenedicarbonylchloride (0.51 g, 2.5 mmol) and anhydrous aluminium chloride (0.8 g, 6 mmol) were stirred under nitrogen in dry dichloromethane (30 cm^3) and ferrocene (1.0 g, 5.4 mmol) in dry dichloromethane (20 cm^3) was added dropwise. The colour of the solution changed to dark blue on addition of ferrocene and an exothermic reaction occurred as the dichloromethane was observed condensing on the walls of the flask and the condenser, the evolution of the HCl gas was also noticed by blue litmus paper. The reaction mixture was refluxed for 10 h and the reaction was followed by TLC; in the beginning one less polar spot and another relatively more polar spot were observed, the less polar spot disappeared by the end of the reaction. The reaction mixture was then poured onto ice water mixture and product was extracted in dichloromethane. The dichloromethane extract was washed with dilute HCl followed by distilled water to completely remove $AlCl_3$ from the product. The organic phase was dried (Na_2SO_4), concentrated and chromatographed over silica gel using dichloromethane as mobile phase to produce 1,3-benzenebis(ferrocenylketone) **82** (1.2 g, 83%) as a red crystalline solid.

Anal. found C 66.8%; H 4.5%; $C_{28}H_{22}Fe_2O_2$ requires C 67.0%; H 4.4%.
$\delta_H(CDCl_3)$ 4.26 (s, 10H, 2 x C_5H_5), [4.65 and 4.95 (t, 4H, 2 x C_5H_4)], [7.60 (t, 1H), 8.10 (d, 2H) and 8.58 (s, 1H) (C_6H_4)].
$\delta_C(CDCl_3)$ 70.3 (s, 2 x C_5H_5), [71.5 (s), 72.8 (s) and 77.7 (s, *ipso*) (2 x C_5H_4)], [128.0 (s), 128.4 (s), 130.9 (s), and 143.2 (s, *ipso*) (C_6H_4)]; and 198.5 (s, 2 x CO).

5.2.5 Synthesis of 1-carbonylchloride-3-ferrocenyl-ketonebenzene.

In order to confirm the reaction intermediate in the above reaction, 1,3-benzenedicarbonylchloride (0.51 g, 2.5 mmol), in CH_2Cl_2 (20 cm^3), was added dropwise to a well-stirred solution of ferrocene (1.0 g, 5.4 mmol) and anhydrous $AlCl_3$ (0.8 g, 6 mmol) in dry CH_2Cl_2 (30 cm^3) at 0 °C. The reaction was monitored by TLC; when it was judged that the abundance of the less-polar product was at a maximum, the reaction mixture was quenched by filtering the reaction mixture onto ice. The organic product was extracted into CH_2Cl_2, and this fraction was washed with water until the washings were neutral. The extract was dried and concentrated, and then chromatographed on silica with 10% petroleum in CH_2Cl_2 as eluent to yield 1-carbonylchloride-3-ferrocenylketonebenzene **81** enough for the NMR characterisation.

$\delta_H(CDCl_3)$ 4.30 (s, 5H, C_5H_5), [4.70 (t, 2H) and 4.90 (t, 2H) (C_5H_4)], [7.66 (d, 1H), 8.18 (d, 1H), 8.32 (d, 1H) and 8.84 (s, 1H) (C_6H_4)].

$\delta_C(CDCl_3)$ 70.4 (s, C_5H_5), [71.5 (s) and 73.2 (s) (C_5H_4) (*ipso* carbon was not visible as that was overlapping with one of the $CDCl_3$

peaks)], [129.4, 130.9, 133.9 and 134.7 (s, C_6H_4)], [133.2 and 140.4 (s, C_6H_4, *ipso*)], 168.0 (s, COCl); 197.4 (s, COFc).

5.2.6 Synthesis of 1,3,5-benzenetris(ferrocenylketone).

In a 100 cm^3 three neck round bottom flask fitted with a condenser, 1,3,5-benzenetricarbonylchloride (0.66 g, 2.5 mmol) and anhydrous aluminium chloride (2 g, 15 mmol) were stirred under nitrogen in dry dichloromethane (50 cm^3) and ferrocene (1.67 g, 9.0 mmol) in dry dichloromethane (50 cm^3) was added dropwise. The colour of the solution changed to dark blue on the addition of ferrocene, evolution of the HCl gas was also noticed by blue litmus paper. The reaction mixture was refluxed overnight and then was poured onto ice water mixture and product was extracted in dichloromethane. The dichloromethane extract was washed with dilute HCl followed by distilled water to completely remove $AlCl_3$ from the product. The organic phase was dried (Na_2SO_4), concentrated and chromatographed over silica gel using dichloromethane as mobile phase to elute unreacted ferrocene (1.1 g) and 1,3,5-benzenetris(ferrocenylketone) **84** (0.5 g, 23% based on the ferrocene consumption) as a red crystalline solid.

$\delta_H(CD_2Cl_2)$ 4.30 (s, 15H, 3 x C_5H_5), [4.70 and 4.95 (t, 6H, 2 x C_5H_4)], and 8.78 (s, 3H) (C_6H_3)].

$\delta_C(CD_2Cl_2)$ 71.2 (s, 3 x C_5H_5), [72.2 (s), 73.8 (s) and 78.7 (s, *ipso*) (3 x C_5H_4)], [131.7 (s), and 140.4 (s, *ipso*) (C_6H_3)], and 198.3 (s, 3 x CO).

5.2.7 Synthesis of ferrocene-containing polyketones.

5.2.7.1 Reaction of ferrocene and 4,4'-biphenyldicarbonylchloride.

In a 500 cm^3 three neck round bottom flask fitted with a condenser, biphenyldicarbonylchloride (5.58 g, 20 mmol), anhydrous aluminium chloride (6.0 g, 45 mmol) and ferrocene (3.72 g, 20 mmol) were stirred under nitrogen in dry dichloromethane (200 cm^3). The colour of the reaction mixture changed to dark blue on addition of ferrocene. The reaction mixture was stirred at 30 °C for 48 h and was further refluxed for 4 h during which time red-powder was precipitated that was filtered out and the filtrate was poured onto ice water sludge. The solid and the dichloromethane extract were washed with dilute HCl followed by distilled water to completely remove $AlCl_3$ from the product. After drying in the oven, the red solid (3.5 g) was found insoluble in most of the organic solvents, but was sparingly soluble in $CDCl_3$. A ^1H NMR of the solid product confirms it as a polymer **85** and the molecular weight of the polymer was estimated *ca.* 1.75 x 10^3 (Appendix XII).

For FCPK **85.**
$\delta_H(CD_3Cl_3)$ 4.28 (s, 5H, C_5H_5), [4.68 and 5.0 (t, 2H, C_5H_4)], and 8.78 (s, 3H) (C_6H_3)].

5.2.7.2 Reaction of ferrocene and 1,3-benzenedicarbonylchloride.

In a 250 cm^3 three neck round bottom flask fitted with a condenser, 1,3-benzenedicarbonylchloride (4.06 g, 20 mmol), anhydrous aluminium chloride (6.0 g, 45 mmol) and ferrocene (3.72 g, 20 mmol) were stirred under nitrogen in dry dichloromethane (150 cm^3). The colour of the

reaction mixture changed to dark blue on addition of ferrocene. The reaction mixture was stirred for 24 h at 30 °C and then was refluxed for 4 h during which time red-powder was precipitated that was filtered out and the filtrate was poured onto ice-water mixture. The solid and the dichloromethane extract were washed with dilute HCl followed by distilled water to completely remove $AlCl_3$ from the product. After drying in the oven, the red solid (2.5 g) was found to be soluble to some extent in $CDCl_3$. The ^1H NMR of the solid product confirms it as a polymer **87** and the molecular weight of the polymer was estimated *ca.* 1.04×10^4 (Appendix XIII). The dichloromethane extract on addition of equal volume light petroleum, precipitated an other batch of red solid. The second batch of red solid was characterised as ferrocene containing ketonic macrocycle (FCKMC) **88** or **89** as it does not have a peak corresponding to unsubstituted Cp ring.

For FCPK **87.**

$\delta_H(CD_3Cl_3)$ 4.20 (s, 5H, C_5H_5), [4.65 and 4.95 (s, 2H, C_5H_4)], 7.52 (s, 1H), 7.95 (s, 2H) and 8.35 (s, 1H) (C_6H_4)].

For FCKMC **88** or **89.**

$\delta_H(CD_2Cl_2)$ [4.60 and 4.95 (s, 2H, C_5H_4)], (s, 1H), (s, 2H) and (s, 1H) (C_6H_4)].

$\delta_C(CD_2Cl_2)$ [73.8 (s, 2C), 75.2 (s, 2C) and 80.0 (s, 1C, *ipso*) (C_5H_4)], 128.6 (s, 1C), 129.1 (s, 1C), 131.9 (s. 2C) and 139.5 (s, 2C, ipso) (C_6H_4)].

The elemental analysis for the above ferrocene-containing polyketones (FCPK) **85** and **87** and ferrocene-containing ketonic macrocycles (FCKMC) **88** or **89** was not according to the calculated values because it is very difficult to get rid of the dichloromethane, light

petroleum ether and the moisture trapped in the huge molecules during work-up that are also visible in the corresponding ^1H NMR spectra.

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Conclusion and Future Work

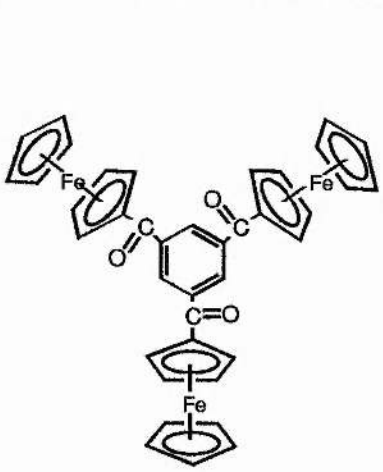
The work carried out in this thesis to explore the ways to synthesise the ferrocene-containing π-conjugated polymers is found to be very interesting and productive and there is a lot of work that could be done as an expansion of this work. There are also some interesting topics that have arised as a result of this work.

1. There is a need to optimise the conditions of polymerization and to find a solvent that can keep the synthesised polymer soluble for a longer period and furnish higher molecular weight polymers.

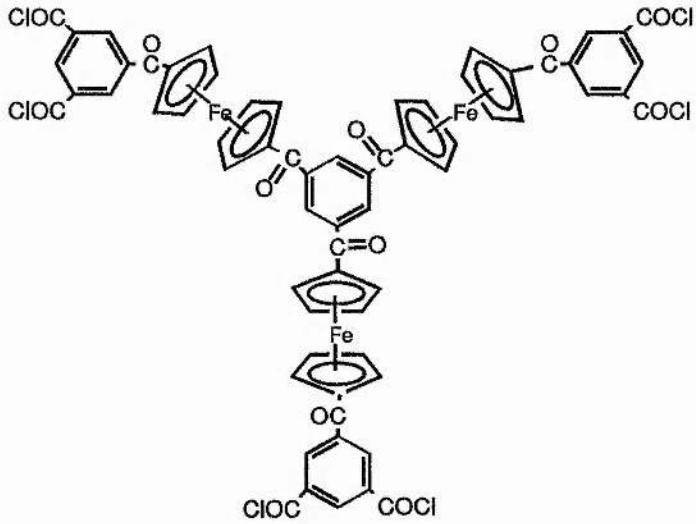
This may be achieved by employing a solvent system which is (a) higher boiling than dichloromethane e.g. 1,1,1 trichloroethane or 1,1,2 trichloroethane or (b) more polar than the chlorinated solvents used e.g. nitrobenzene or even DMF or DMAc provided they themselves do not enter into the reaction.

2. The π-conjugated polymers and their small analogues produced in this work need to be studied for their electrical properties: for example the cyclic voltammetric studies of these polymers may be carried out by depositing a thin film on the electrode, and conductance behaviour may be studied by making compressed pellets and then measuring their conductance. The study of the effect of substituents on organic monomers or doping the polymer with some oxidising agent such as iodine to oxidise some of the iron atoms in the ferrocene moieties to Fe^{3+}, hence producing holes in the system, will also be interesting.

3. Benzene-1,3,5-tricarbonyl chloride that yields 1,3,5-tris-(ferrocenylketone)benzene **84** in a Friedel Crafts reaction with ferrocene, can be used as a starting point to produce the dendrimer polymers of n^{th} generation by stepwise acylation and isolation of the product at each step. For example the structures of the first and the second generation molecules are shown below.

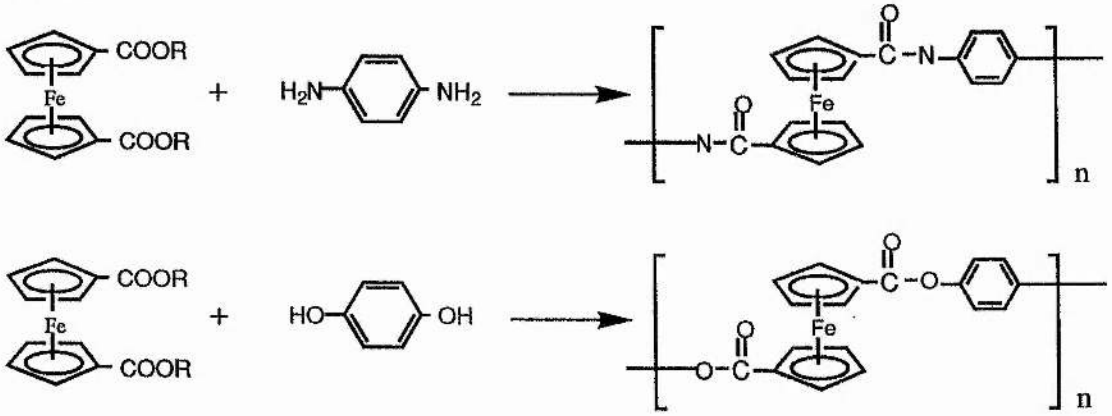


First generation



Second generation

4. Some more π-conjugated ferrocene-containing products may be synthesised such as ferrocene-containing polyamides and ferrocene-containing polyesters by using the appropriate monomers as shown below.



(Where R = H, Alkyl or Aryl)

APPENDICES

APPENDIX I

Thermodynamic calculations to show that (α-ferrocenylphenacyl)-triphenylphosphonium iodide (38a) is the sole thermodynamically possible product.

Prior to the crystallization of **38a** the ions present in the solution are $[FcCH(COPh)PPh_3]^+$, I^-, Li^+ and Cl^- and the following equilibrium must be considered:

$$Li^+Cl^- + [FcCH(COPh)PPh_3]^+I^- \rightleftharpoons Li^+I^- + [FcCH(COPh)PPh_3]^+Cl^- \quad (i)$$

For simplicity let us assume

Li = A, Cl = X, $[FcCH(COPh)PPh_3]$ = B and I = Y

where A & X are small entities and B & Y are large entities.

Therefore the above equation becomes:

$$A^+X^- + B^+Y^- \rightleftharpoons A^+Y^- + B^+X^- \quad (ii)$$

If we consider the lattice energy (U), the energy released when a crystal lattice is formed from the ions in gasious state, for the formation of the above compounds and

$$U = \frac{k}{r^+ + r^-}$$

(where r^+ is the radius of the cation and r^- is the radius of the anion and k is the constant of proportionality.)

The heat of formation of $[FcCH(COPh)PPh_3]^+I^-$ and LiCl, (LHS) in the above equilibrium can be written as:

$$\Delta H_f^{\phi} = U_{(AX)} + U_{(BY)} - U_{(AY)} - U_{(BX)}$$

$$\Delta H_f^{\phi} = \frac{k}{r_A + r_X} + \frac{k}{r_B + r_Y} - \frac{k}{r_A + r_Y} - \frac{k}{r_B + r_X}$$

$$= k\left[\frac{1}{r_A + r_X} - \frac{1}{r_A + r_Y}\right] - k\left[\frac{1}{r_B + r_X} - \frac{1}{r_B + r_Y}\right]$$

$$= k\left[\frac{(r_A + r_Y) - (r_A + r_X)}{(r_A + r_X)(r_A + r_Y)}\right] - k\left[\frac{(r_B + r_Y) - (r_B + r_X)}{(r_B + r_X)(r_B + r_Y)}\right]$$

$$\Delta H_f^{\phi} = k\left[\frac{(r_Y - r_X)}{(r_A + r_X)(r_A + r_Y)}\right] - k\left[\frac{(r_Y - r_X)}{(r_B + r_X)(r_B + r_Y)}\right]$$

$$= k\,(r_Y - r_X)\left[\frac{1}{(r_A + r_X)(r_A + r_Y)} - \frac{1}{(r_B + r_X)(r_B + r_Y)}\right]$$

$$= k\,(r_Y - r_X)\left[\frac{(r_B + r_X)(r_B + r_Y) - (r_A + r_X)(r_A + r_Y)}{(r_A + r_X)(r_A + r_Y)(r_B + r_X)(r_B + r_Y)}\right]$$

$$= k\,(r_Y - r_X)\left[\frac{r_B^2 + r_B r_Y + r_B r_X + \cancel{r_X r_Y} - r_A^2 - r_A r_Y - r_A r_X - \cancel{r_X r_Y}}{(r_A + r_X)(r_A + r_Y)(r_B + r_X)(r_B + r_Y)}\right]$$

$$= k\,(r_Y - r_X)\left[\frac{r_B^2 - r_A^2 + r_B r_Y - r_A r_Y + r_B r_X - r_A r_X}{(r_A + r_X)(r_A + r_Y)(r_B + r_X)(r_B + r_Y)}\right]$$

$$= k\,(r_Y - r_X)\left[\frac{(r_B - r_A)(r_B + r_A) + r_Y(r_B - r_A) + r_X(r_B - r_A)}{(r_A + r_X)(r_A + r_Y)(r_B + r_X)(r_B + r_Y)}\right]$$

$$= k\,(r_Y - r_X)(r_B - r_A)\left[\frac{r_B + r_A + r_Y + r_X}{(r_A + r_X)(r_A + r_Y)(r_B + r_X)(r_B + r_Y)}\right]$$

As B and Y are big entities (ions) and A and X are small entities (ions) the solution of the above equation will be a positive number (ΔH_f^{ϕ} = +ve) so the left hand side of equation (i) will be thermodynamically more favoured and the right hand side will be thermodynamically less favored. As all the four compounds in the equilibrium (i) are solid so there will not be any significant change in entropy of the system for the cryatallization of any pair of compounds. Hence the only thermodynamically possible products formed from the given mixture of ions will be $[FcCH(COPh)PPh_3]^+I^-$ and LiCl.

If we take a simple example when small ions (A = X = 1 Å) and the large ions (B = Y = 5 Å) the lattice energy for the pair of compounds on LHS of equation (i) will be (3/5)k and that for the RHS will calculate to (1/3)k, again showing that the pair of compounds on the LHS is more stable than that on RHS.

APPENDIX II*

Crystallographic data for (α-ferrocenylphenacyl)triphenylphosphonium iodide (38a)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{36}H_{30}FeIOP$
Formula Weight	692.32
Crystal Colour, Habit	red, triangular-shaped plates
Crystal Dimensions	0.39 X 0.39 X 0.29 mm
Crystal System	orthorhombic
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (9.20 - 14.35°)
Omega Scan Peak Width at Half-height	0.°
Lattice Parameters	a = 16.949(2)Å b = 17.907(2) Å c = 19.662(3) Å α = 90.00° β = 90.00° γ = 90.00° V = 5967.7(13) Å^3
Space Group	Pbca
Z value	8
D_{calc}	Not measured
D_x	1.541 Mg m^{-3}
F(000)	2784
$\mu(M_o K_\alpha)$	1.621 mm^{-1}

* Following the university restriction for the size of thesis only selected data are presented here, for the detailed account of atomic coordinates, geometric parameters and anisotropic factors pleases refer to **Cambridge Crystallographic Database** ref. *Acta Crystallogr. C*, 1996, **52**, 1634.

B. Intensity Measurements

Diffractometer	Enraf-Nonius CAD-4
Radiation	$M_o K_\alpha$ (λ = 0.7107 Å) graphite monochromated
Temperature	294 (1) K
Scan Type	$\theta/2\theta$
θ_{max}	26.9°
	h = 0-21
	k = 0-22
	l = 0-25
No. of Reflections Measured	Total: 6473
	Observed: 2270
Absorption Correction	5 ψ-scans at 4° steps
3 standard reflections	frequency: 120 min
	intensity decay: 3.0%

C. Structure Solution and Refinement

Structure Solution	Patterson heavy-atom method and NRCVAX94
Refinement	NRCVAX94 and SHELXL93
Refinement on F^2	$R[F^2 > 2\sigma(F^2)]$ = 0.0552
	$\omega R(F^2)$ = 0.0911
	S = 1.151
Number of Reflections	6473
Number of parameters	361
Riding (SHELXL defaults, C-H 0.93 to 0.98 Å)	
$w = 1/[\sigma^2 (F_o^2) + (0.0371\ P)^2]$ where $P = (Fo^2 + 2Fc^2)/3$	
Max Shift/Error in Final Cycle $(\Delta/\sigma)_{max}$	< 0.001
Maximum peak in Final Diff. Map (ΔP_{max})	0.509 $e^-/Å^3$
Minimum peak in Final Diff. Map (ΔP_{min})	-0.406 $e^-/Å^3$

Table 1. Fractional Atomic coordinates and equivalent isotropic displacement parameters (Å^2)

atom	x	y	z	U_{eq}
I1	0.60568(3)	0.17123(3)	0.01255(2)	0.0576(2)
Fe1	0.90153(6)	0.12833(6)	0.02802(4)	0.0443(3)
P1	0.75766(10)	0.06276(10)	0.22992(8)	0.0333(4)
O2	0.8637(3)	-0.0511(3)	0.1456(3)	0.0621(15)
C1	0.7875(3)	0.0611(3)	0.1397(2)	0.031(2)
C2	0.8066(4)	-0.0205(4)	0.1205(3)	0.047(2)
C11	0.8558(4)	0.1113(4)	0.1226(3)	0.037(2)
C12	0.8505(4)	0.1880(3)	0.1042(3)	0.043(2)
C13	0.9289(5)	0.2153(4)	0.0922(3)	0.056(2)
C14	0.9791(5)	0.1553(5)	0.1020(4)	0.062(2)
C15	0.9372(4)	0.0914(4)	0.1216(3)	0.47(2)
Cp1	0.9103(5)	0.1523(4)	0.1085(3)	0.
C21	0.8349(5)	0.0759(5)	-0.0436(3)	0.060(2)
C22	0.8430(6)	0.1505(5)	-0.0595(4)	0.067(3)
C23	0.9235(6)	0.1663(5)	-0.0676(3)	0.071(3)
C24	0.9631(5)	0.0995(6)	-0.0565(4)	0.73(3)
C25	0.9099(6)	0.0436(5)	-0.0414(4)	0.070(3)
Cp2	0.8949(6)	0.1072(5)	-0.0537(4)	0.
C31	0.7534(5)	-0.0620(4)	0.0728(3)	0.045(2)
C32	0.7827(5)	-0.1256(4)	0.0435(3)	0.051(2)
C33	0.7343(6)	-0.1655(5)	0.0005(4)	0.074(3)
C34	0.6585(7)	-0.1444(5)	-0.0105(4)	0.080(3)
C35	0.6287(5)	-0.0818(5)	0.0204(4)	0.070(2)
C36	0.6767(4)	-0.0393(4)	0.0604(4)	0.055(2)
C41	0.8410(4)	0.0554(4)	0.2852(3)	0.038(2)
C42	0.8961(4)	0.1120(4)	0.2853(3)	0.046(2)
C43	0.9606(4)	0.1093(5)	0.3285(4)	0.055(2)
C44	0.9696(5)	0.0488(5)	0.3699(4)	0.063(2)
C45	0.9165(5)	-0.0075(5)	0.3718(4)	0.065(2)
C46	0.8498(4)	-0.0046(4)	0.3299(4)	0.055(2)
C51	0.6887(4)	-0.0115(4)	0.2447(3)	0.035(2)
C52	0.7106(4)	-0.0865(4)	0.2373(3)	0.051(2)
C53	0.6559(5)	-0.1433(4)	0.2460(4)	0.065(2)
C54	0.5798(5)	-0.1253(5)	0.2593(4)	0.068(3)
C55	0.5571(4)	-0.0526(5)	0.2663(4)	0.061(2)
C56	0.6103(5)	0.0035(4)	0.2601(3)	0.046(2)
C61	0.7112(3)	0.1503(3)	0.2479(3)	0.033(2)
C62	0.6722(4)	0.1907(4)	0.1981(3)	0.046(2)
C63	0.6320(4)	0.2561(4)	0.2149(4)	0.055(2)
C64	0.6305(4)	0.2797(4)	0.2812(5)	0.062(2)
C65	0.6680(5)	0.2397(5)	0.3313(4)	0.063(2)
C66	0.7087(4)	0.1753(4)	0.3154(3)	0.053(2)

$$U_{eq} = (1/3)\ \Sigma_i\ \Sigma_j\ U_{ij}\ a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$$

Table 2. Selected Bond Lengths (Å)

atom	atom/moiety	distance	atom	atom	distance
Fe1	Cp1	1.646(7)	C11	C12	1.424(8)
Fe1	Cp2	1.655(7)	C11	C15	1.425(8)
P1	C1	1.845(6)	C12	C13	1.436(9)
P1	C41	1.788(6)	C13	C14	1.384(9)
P1	C51	1.794(7)	C14	C15	1.402(9)
P1	C61	1.790(6)	C21	C22	1.380(10)
O2	C2	1.217(7)	C21	C25	1.397(10)
C1	C2	1.545(8)	C22	C23	1.403(10)
C1	C11	1.504(8)	C23	C24	1.389(10)
C2	C31	1.498(9)	C24	C25	1.380(10)

Table 3. Selected Bond Angles(°)

atom/ moiety	atom/ moiety	atom/ moiety	angle	atom/ moiety	atom/ moiety	atom/ moiety	angle
Cp1	Fe1	Cp2	177.7(3)	P1	C1	C2	107.9(4)
C41	P1	C51	111.2(3)	P1	C1	C11	114.6(4)
C41	P1	C61	107.0(3)	C2	C1	C11	110.4(5)
C61	P1	C51	109.3(3)	O2	C2	C1	119.6(6)
C1	P1	C61	108.9(3)	O2	C2	C31	120.7(7)
C1	P1	C51	108.8(3)	C1	C2	C31	119.7(6)
C1	P1	C41	111.5(3)				

Table 4. Selected Torsion Angles(°)

atom	atom	atom	atom	angle
C41	P1	C1	C11	-46.5(6)
C51	P1	C1	C11	-169.6(5)
C61	P1	C1	C11	71.4(5)
C11	C1	C2	O2	58.6(8)
P1	C1	C2	O2	-67.4(7)
C11	C1	C2	C31	-123.4(6)
P1	C1	C2	C31	110.7(6)

APPENDIX III*

Crystallographic data for 2-ferrocenyl-1-biphenyl-1-ethanone (39b)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{24}H_{20}FeO$
Formula Weight	380.27
Crystal Colour, Habit	orange, plate
Crystal Dimensions	0.35 X 0.25 X 0.05 mm
Crystal System	monoclinic
Lattice Type	C-centred
No. of Reflections Used for Unit Cell Determination (2θ range)	11 (6.5 - 15.6°)
Omega Scan Peak Width at Half-height	0.38°
Lattice Parameters	a = 42.64(1)Å b = 10.493(8) Å c = 7.88(1) Å β = 93.3(1)° V = 3521(6) Å^3
Space Group	C2/c (No. 15)
Z value	8
D_{calc}	1.434 g/cm^3
F(000)	1584.00
$\mu(M_o K_\alpha)$	8.65 cm^{-1}

* Following the university restriction for the size of thesis only selected data are presented here, for the detailed account of atomic coordinates, geometric parameters and anisotropic factors pleases refer to **Cambridge Crystallographic Database** ref. *J. Organomet. Chem.*, 1997, **542**, 81.

B. Intensity Measurements

Diffractometer	Rigaku AFC7S
Radiation	M_o K_α (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 8.53)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	235 mm
Temperature	22.0 °C
Scan Type	ω-2θ
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	(1.78 + 0.35 tan θ)°
$2\theta_{max}$	45.1°
No. of Reflections Measured	Total: 2496 Unique: 2458 (R_{int} = 0.018)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\omega$ (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0030
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00 σ(I))	1484
No. Variables	105
Reflection/Parameter Ratio	14.13
Residuals: R; Rw	0.111 ; 0.093
Goodness of Fit Indicator	6.51
Max Shift/Error in Final Cycle	0.20
Maximum peak in Final Diff. Map	1.30 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.95 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe(1)	0.55865(6)	0.2572(3)	0.1281(3)	2.86(5)
O(1)	0.6397(3)	0.471(1)	0.464(1)	4.3(3)
C(1)	0.5953(4)	0.339(1)	0.270(2)	2.8(3)
C(2)	0.5721(4)	0.282(2)	0.377(2)	3.3(4)
C(3)	0.5416(4)	0.339(2)	0.344(2)	3.6(4)
C(4)	0.5458(4)	0.434(2)	0.213(2)	3.5(4)
C(5)	0.5782(4)	0.434(1)	0.173(2)	2.5(3)
C(6)	0.5788(5)	0.123(2)	-0.011(2)	4.7(5)
C(7)	0.5535(5)	0.070(2)	0.079(2)	4.5(4)
C(8)	0.5255(5)	0.129(2)	0.038(2)	4.8(5)
C(9)	0.5314(5)	0.219(2)	-0.090(2)	5.2(5)
C(10)	0.5634(4)	0.220(2)	-0.120(2)	4.2(4)
C(11)	0.6275(4)	0.307(1)	0.262(2)	2.6(3)
C(12)	0.6499(4)	0.388(1)	0.368(2)	2.8(4)
C(13)	0.6842(4)	0.375(1)	0.360(2)	2.1(3)
C(14)	0.6994(4)	0.287(2)	0.256(2)	3.2(4)
C(15)	0.7310(4)	0.280(1)	0.247(2)	2.5(3)
C(16)	0.7508(4)	0.363(1)	0.337(2)	2.1(3)
C(17)	0.7373(4)	0.446(1)	0.447(2)	2.7(3)
C(18)	0.7057(4)	0.453(2)	0.455(2)	2.9(4)
C(19)	0.7842(4)	0.359(1)	0.325(2)	2.1(3)
C(20)	0.7996(4)	0.266(2)	0.232(2)	3.1(3)
C(21)	0.8321(4)	0.264(2)	0.225(2)	3.4(3)
C(22)	0.8520(4)	0.353(2)	0.306(2)	3.4(4)
C(23)	0.8372(4)	0.445(2)	0.398(2)	3.9(4)
C(24)	0.8046(4)	0.447(2)	0.408(2)	3.3(4)

$$B_{eq} = 8/3\ \pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha]$$

Table 2. Selected Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	C(12)	1.25(2)	C(1)	C(2)	1.46(2)
C(1)	C(5)	1.43(2)	C(1)	C(11)	1.42(2)
C(2)	C(3)	1.44(2)	C(3)	C(4)	1.45(2)
C(4)	C(5)	1.44(2)	C(6)	C(7)	1.43(2)
C(6)	C(10)	1.47(2)	C(7)	C(8)	1.37(2)
C(8)	C(9)	1.41(2)	C(9)	C(10)	1.40(2)
C(11)	C(12)	1.50(2)	C(12)	C(13)	1.47(2)
C(13)	C(14)	1.42(2)	C(13)	C(18)	1.41(2)
C(14)	C(15)	1.36(2)	C(15)	C(16)	1.38(2)
C(16)	C(17)	1.38(2)	C(16)	C(19)	1.44(2)
C(17)	C(18)	1.36(2)	C(19)	C(20)	1.40(2)
C(19)	C(24)	1.40(2)	C(20)	C(21)	1.39(2)
C(21)	C(22)	1.39(2)	C(22)	C(23)	1.38(2)
C(23)	C(24)	1.40(2)			

Table 3. Selected Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(1)	C(5)	104(1)	C(2)	C(1)	C(11)	128(1)
C(5)	C(1)	C(11)	127(1)	C(1)	C(2)	C(3)	111(1)
C(2)	C(3)	C(4)	105(1)	C(3)	C(4)	C(5)	108(1)
C(1)	C(5)	C(4)	110(1)	C(7)	C(6)	C(10)	103(1)
C(6)	C(7)	C(8)	112(1)	C(7)	C(8)	C(9)	106(1)
C(8)	C(9)	C(10)	109(1)	C(6)	C(10)	C(9)	107(1)
C(1)	C(11)	C(12)	115(1)	O(1)	C(12)	C(11)	120(1)
O(1)	C(12)	C(13)	118(1)	C(11)	C(12)	C(13)	121(1)
C(12)	C(13)	C(14)	124(1)	C(12)	C(13)	C(18)	122(1)
C(14)	C(13)	C(18)	112(1)	C(13)	C(14)	C(15)	123(1)
C(14)	C(15)	C(16)	121(1)	C(15)	C(16)	C(17)	117(1)
C(15)	C(16)	C(19)	121(1)	C(17)	C(16)	C(19)	120(1)
C(16)	C(17)	C(18)	120(1)	C(13)	C(18)	C(17)	124(1)
C(16)	C(19)	C(20)	123(1)	C(16)	C(19)	C(24)	122(1)
C(20)	C(19)	C(24)	113(1)	C(19)	C(20)	C(21)	121(1)
C(20)	C(21)	C(22)	123(1)	C(21)	C(22)	C(23)	114(1)
C(22)	C(23)	C(24)	121(1)	C(19)	C(24)	C(23)	123(1)
C(1)	C(11)	H(11)	106.4	C(12)	C(11)	H(11)	107.8

Table 4. Selected Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	C(12)	C(11)	C(1)	4(2)	O(1)	C(12)	C(13)	C(14)	-179(1)
O(1)	C(12)	C(13)	C(18)	0(2)	C(1)	C(11)	C(12)	C(13)	-173(1)
C(2)	C(1)	C(11)	C(12)	-95(1)	C(3)	C(2)	C(1)	C(11)	-178(1)
C(4)	C(5)	C(1)	C(11)	177(1)	C(5)	C(1)	C(11)	C(12)	84(1)
C(11)	C(12)	C(13)	C(14)	0(2)	C(11)	C(12)	C(13)	C(18)	178(1)
C(12)	C(13)	C(14)	C(15)	177(1)	C(12)	C(13)	C(18)	C(17)	-177(1)

APPENDIX IV*

Crystallographic data for ferrocenylbiphenylethanedione (40b)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{24}H_{18}FeO_2$
Formula Weight	394.25
Crystal Colour, Habit	red, plate
Crystal Dimensions	0.50 X 0.40 X 0.05 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (23.9 - 25.0°)
Omega Scan Peak Width at Half-height	0.33°
Lattice Parameters	a = 9.900(3)Å b = 24.423(4) Å c = 7.496(3) Å V = 1812.6(9) Å^3
Space Group	$P2_12_12_1$ (No. 19)
Z value	4
D_{calc}	1.445 g/cm^3
F(000)	816.00
$\mu(M_o K_\alpha)$	8.45 cm^{-1}

* Following the university restriction for the size of thesis only selected data are presented here, for the detailed account of atomic coordinates, geometric parameters and anisotropic factors pleases refer to **Cambridge Crystallographic Database** ref. *J. Organomet. Chem.*, 1997, **530**, 177.

B. Intensity Measurements

Diffractometer	Rigaku AFC7S
Radiation	$M_o K_\alpha$ (λ =0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 8.53)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	235 mm
Temperature	20.0 °C
Scan Type	ω
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	(1.73 + 0.35 tan θ)°
$2\theta_{max}$	50.0°
No. of Reflections Measured	Total: 2374 Unique: 1876 (R_{int} = 0.034)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.8241 - 1.0000)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\omega$ (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0010
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00 σ(I))	1342
No. Variables	244
Reflection/Parameter Ratio	5.50
Residuals: R; Rw	0.040 ; 0.030
Goodness of Fit Indicator	1.93
Max Shift/Error in Final Cycle	0.01
Maximum peak in Final Diff. Map	0.22 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.21 $e^-/Å^3$

Table 1. Selected Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe(1)	1.0076(1)	0.03666(4)	0.3332(1)	3.55(2)
O(1)	1.1815(7)	0.1501(2)	0.0568(7)	8.0(2)
O(2)	1.4318(5)	0.0993(2)	0.2744(7)	6.6(2)
C(1)	1.1578(6)	0.0585(3)	0.1636(9)	3.6(1)
C(2)	1.2002(6)	0.0144(3)	0.2705(8)	3.7(2)
C(3)	1.1130(6)	-0.0302(3)	0.2404(9)	4.3(2)
C(4)	1.0163(7)	-0.0137(3)	0.1150(9)	4.6(2)
C(5)	1.0407(7)	0.0412(3)	0.0661(8)	4.4(2)
C(6)	0.9211(8)	0.1030(3)	0.449(1)	5.6(2)
C(7)	1.0014(10)	0.0746(3)	0.5750(8)	5.7(2)
C(8)	0.9499(8)	0.0220(3)	0.5875(10)	5.7(2)
C(9)	0.8379(8)	0.0166(3)	0.472(1)	5.2(2)
C(10)	0.8201(8)	0.0670(4)	0.3885(10)	5.4(2)
C(11)	1.2129(7)	0.1139(3)	0.1613(10)	4.7(2)
C(12)	1.3269(8)	0.1256(3)	0.292(1)	5.2(2)
C(13)	1.3122(7)	0.1677(3)	0.4353(10)	4.3(2)
C(14)	1.2029(9)	0.2013(3)	0.446(1)	7.6(3)
C(15)	1.1890(9)	0.2374(3)	0.586(1)	7.8(3)
C(16)	1.2874(7)	0.2428(3)	0.7174(10)	4.6(2)
C(17)	1.3952(7)	0.2078(3)	0.703(1)	5.2(2)
C(18)	1.4096(7)	0.1710(3)	0.565(1)	5.4(2)
C(19)	1.2721(8)	0.2817(3)	0.869(1)	4.7(2)
C(20)	1.1698(7)	0.3192(3)	0.8754(10)	5.3(2)
C(21)	1.1592(8)	0.3561(3)	1.016(1)	5.9(2)
C(22)	1.2484(9)	0.3553(3)	1.152(1)	6.3(2)
C(23)	1.350(1)	0.3185(4)	1.149(1)	10.9(4)
C(24)	1.359(1)	0.2822(4)	1.008(2)	11.1(4)

$$B_{eq} = 8/3\ \pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha]$$

Table 2. Selected Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	C(11)	1.221(8)	O(2)	C(12)	1.228(8)
C(1)	C(2)	1.408(8)	C(1)	C(5)	1.434(8)
C(1)	C(11)	1.458(8)	C(2)	C(3)	1.407(8)
C(3)	C(4)	1.401(9)	C(4)	C(5)	1.409(9)
C(6)	C(7)	1.414(9)	C(6)	C(10)	1.408(10)
C(7)	C(8)	1.385(10)	C(8)	C(9)	1.412(10)
C(9)	C(10)	1.392(9)	C(11)	C(12)	1.521(10)
C(12)	C(13)	1.494(9)	C(13)	C(14)	1.360(10)
C(13)	C(18)	1.372(9)	C(14)	C(15)	1.375(10)
C(15)	C(16)	1.393(10)	C(16)	C(17)	1.372(9)
C(16)	C(19)	1.489(9)	C(17)	C(18)	1.380(9)
C(19)	C(20)	1.367(9)	C(19)	C(24)	1.36(1)
C(20)	C(21)	1.390(9)	C(21)	C(22)	1.35(1)
C(22)	C(23)	1.35(1)	C(23)	C(24)	1.38(1)

Table 3. Selected Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	C(11)	C(1)	125.7(8)	O(1)	C(11)	C(12)	117.8(7)
C(1)	C(11)	C(12)	116.4(7)	O(2)	C(12)	C(11)	117.4(7)
O(2)	C(12)	C(13)	121.3(8)	C(11)	C(12)	C(13)	121.3(7)
C(12)	C(13)	C(14)	122.4(7)	C(12)	C(13)	C(18)	118.7(7)
C(16)	C(19)	C(20)	122.0(7)	C(16)	C(19)	C(24)	122.0(7)

Table 4. Selected Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	C(11)	C(12)	O(2)	-113.3(9)	O(1)	C(11)	C(12)	C(13)	66.3(9)
O(2)	C(12)	C(11)	C(1)	62.1(9)	C(1)	C(11)	C(12)	C(13)	-118.2(7)
C(2)	C(1)	C(11)	C(12)	-1(1)	C(5)	C(1)	C(11)	C(12)	172.6(6)
C(11)	C(12)	C(13)	C(14)	-6(1)	C(11)	C(12)	C(13)	C(18)	170.5(7)
C(14)	C(15)	C(16)	C(19)	-179.7(8)	C(15)	C(16)	C(19)	C(20)	-8(1)
C(15)	C(16)	C(19)	C(24)	171(1)	C(16)	C(19)	C(20)	C(21)	-178.3(7)
C(16)	C(19)	C(24)	C(23)	178(1)	C(17)	C(16)	C(19)	C(20)	175.1(7)
C(17)	C(16)	C(19)	C(24)	-4(1)	C(18)	C(17)	C(16)	C(19)	179.0(7)

APPENDIX U*

Crystallographic data for *racemic* 2,3-diferrocenyl-1,4-diphenylbutane-1,4-dione (42a)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{36}H_{30}Fe_2O_2$
Formula Weight	606.33
Crystal Colour, Habit	yellow, needle
Crystal Dimensions	0.07 X 0.07 X 0.30 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (15.0 - 25.0°)
Omega Scan Peak Width at Half-height	0.29°
Lattice Parameters	a = 14.888(4)Å b = 18.583(6) Å c = 10.679(8) Å α = 90.80(4)° β = 90.50(4)° γ = 72.44(2)°
	V = 2816(2) Å^3
Space Group	$P\bar{1}$ (No. 2)
Z value	4
D_{calc}	1.430 g/cm^3
F(000)	1256.00
$\mu(M_o K_\alpha)$	10.61 cm^{-1}

* Following the university restriction for the size of thesis only selected data are presented here, for the detailed account of atomic coordinates, geometric parameters and anisotropic factors pleases refer to **Cambridge Crystallographic Database** ref. *J. Organomet. Chem.*, 1997, **542**, 81.

B. Intensity Measurements

Diffractometer	Rigaku AFC7S
Radiation	$M_o K_\alpha$ (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 8.53)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	235 mm
Temperature	20.0 °C
Scan Type	ω-2θ
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	(0.94 + 0.35 tan θ)°
$2\theta_{max}$	50.2°
No. of Reflections Measured	Total: 10216 Unique: 9797 (R_{int} = 0.141)
Corrections	Lorentz-polarization Secondary
Extinction	(coefficient: 2.00257e-07)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\omega$ (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0040
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00sigma(I))	5896
No. Variables	722
Reflection/Parameter Ratio	8.17
Residuals: R; Rw	0.049 ; 0.052
Goodness of Fit Indicator	2.28
Max Shift/Error in Final Cycle	0.05
Maximum peak in Final Diff. Map	0.38 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.43 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe(11)	0.34916(7)	0.33130(6)	0.83940(9)	3.21(2)
Fe(12)	0.11579(7)	0.34729(6)	1.38982(9)	3.18(2)
Fe(21)	-0.15868(6)	0.35936(6)	0.89522(9)	2.98(2)
Fe(22)	-0.39082(7)	0.36774(6)	0.34839(9)	3.46(3)
O(11)	0.3347(3)	0.1432(3)	1.3004(5)	5.3(1)
O(12)	0.2953(4)	0.1294(3)	0.9669(5)	5.4(2)
O(21)	-0.2259(4)	0.1567(3)	0.7745(5)	5.4(2)
O(22)	-0.1668(4)	0.1679(3)	0.4319(5)	6.0(2)
C(11)	0.2572(5)	0.1645(4)	1.2517(6)	3.5(2)
C(12)	0.2342(4)	0.2318(4)	1.1654(6)	2.9(2)
C(13)	0.3216(4)	0.2303(4)	1.0849(6)	2.8(1)
C(14)	0.3533(5)	0.1577(4)	1.0085(6)	3.3(2)
C(21)	-0.1639(5)	0.1799(4)	0.7347(6)	3.4(2)
C(22)	-0.1895(4)	0.2513(4)	0.6586(6)	2.8(2)
C(23)	-0.2722(4)	0.2533(4)	0.5685(6)	2.9(2)
C(24)	-0.2436(5)	0.1846(4)	0.4797(6)	3.6(2)
C(111)	0.2029(4)	0.3051(4)	1.2369(5)	2.8(2)
C(112)	0.2519(5)	0.3291(4)	1.3344(6)	3.9(2)
C(113)	0.2070(5)	0.4078(4)	1.3623(7)	4.2(2)
C(114)	0.1307(5)	0.4306(4)	1.2786(7)	4.5(2)
C(115)	0.1263(5)	0.3690(4)	1.2035(6)	3.5(2)
C(121)	0.0091(7)	0.3034(7)	1.4244(9)	6.8(3)
C(122)	0.0869(7)	0.2662(5)	1.4933(9)	6.0(3)
C(123)	0.1094(7)	0.3195(7)	1.5721(7)	6.0(3)
C(124)	0.0442(8)	0.3894(6)	1.5508(9)	6.0(3)
C(125)	-0.0169(6)	0.3812(7)	1.462(1)	6.9(3)
C(131)	0.2964(4)	0.2988(4)	1.0028(6)	2.9(2)
C(132)	0.2286(4)	0.3140(4)	0.9033(6)	3.5(2)
C(133)	0.2122(5)	0.3911(4)	0.8672(7)	4.3(2)
C(134)	0.2707(5)	0.4212(4)	0.9419(7)	4.1(2)
C(135)	0.3222(5)	0.3654(4)	1.0229(6)	3.5(2)
C(141)	0.456(1)	0.2482(6)	0.759(1)	8.6(4)
C(142)	0.3853(9)	0.2794(8)	0.6708(10)	7.7(4)
C(143)	0.3764(7)	0.3522(7)	0.6612(8)	6.3(3)
C(144)	0.4347(9)	0.3726(6)	0.740(1)	7.5(4)
C(145)	0.4872(6)	0.306(1)	0.800(1)	9.4(4)
C(151)	0.1846(5)	0.1254(4)	1.2754(6)	3.3(2)
C(152)	0.2059(5)	0.0663(4)	1.3579(7)	4.9(2)
C(153)	0.1387(7)	0.0304(4)	1.3866(8)	5.9(3)
C(154)	0.0513(7)	0.0541(5)	1.3346(9)	5.8(3)
C(155)	0.0302(6)	0.1111(5)	1.2518(8)	5.6(2)
C(156)	0.0961(5)	0.1474(4)	1.2224(7)	4.6(2)
C(161)	0.4557(5)	0.1235(4)	0.9795(6)	3.2(2)
C(162)	0.4806(5)	0.0678(4)	0.8863(8)	4.9(2)
C(163)	0.5733(6)	0.0366(5)	0.8522(8)	5.4(2)
C(164)	0.6418(6)	0.0607(5)	0.9073(8)	5.5(2)
C(165)	0.6181(6)	0.1145(5)	1.0009(9)	6.8(3)
C(166)	0.5254(5)	0.1467(5)	1.0356(7)	5.1(2)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C(211)	-0.2173(4)	0.3193(4)	0.7415(6)	2.8(2)
C(212)	-0.2764(5)	0.3298(4)	0.8489(6)	3.5(2)
C(213)	-0.3008(5)	0.4073(4)	0.8883(7)	4.1(2)
C(214)	-0.2564(5)	0.4436(4)	0.8065(7)	3.7(2)
C(215)	-0.2046(5)	0.3902(4)	0.7168(6)	3.3(2)
C(221)	-0.0281(6)	0.2886(5)	0.9376(9)	5.7(2)
C(222)	-0.0879(7)	0.2976(6)	1.0401(9)	6.4(3)
C(223)	-0.1178(6)	0.3739(6)	1.0728(7)	5.7(2)
C(224)	-0.0802(6)	0.4137(5)	0.9944(9)	5.3(2)
C(225)	-0.0239(5)	0.3623(6)	0.9113(8)	5.7(3)
C(231)	-0.3000(4)	0.3262(4)	0.4978(6)	2.9(2)
C(232)	-0.3729(4)	0.3922(4)	0.5326(6)	3.1(2)
C(233)	-0.3695(5)	0.4523(4)	0.4577(7)	3.8(2)
C(234)	-0.2959(5)	0.4269(5)	0.3754(7)	4.7(2)
C(235)	-0.2529(5)	0.3476(4)	0.3966(6)	3.9(2)
C(241)	-0.425(1)	0.2866(6)	0.250(1)	8.0(4)
C(242)	-0.496(1)	0.322(1)	0.321(1)	11.3(6)
C(243)	-0.5222(7)	0.4006(9)	0.281(1)	9.2(4)
C(244)	-0.4641(10)	0.4023(7)	0.186(1)	7.5(3)
C(245)	-0.4054(7)	0.3342(9)	0.1713(9)	7.3(3)
C(251)	-0.0640(5)	0.1410(4)	0.7668(6)	3.3(2)
C(252)	-0.0437(5)	0.1013(4)	0.8765(7)	4.5(2)
C(253)	0.0488(6)	0.0668(4)	0.9129(8)	5.2(2)
C(254)	0.1212(6)	0.0714(5)	0.8404(9)	5.4(2)
C(255)	0.1020(6)	0.1075(5)	0.7289(8)	5.9(2)
C(256)	0.0099(5)	0.1425(4)	0.6919(7)	4.4(2)
C(261)	-0.3108(5)	0.1404(4)	0.4531(6)	3.3(2)
C(262)	-0.2894(5)	0.0882(5)	0.3569(7)	5.0(2)
C(263)	-0.3493(7)	0.0454(5)	0.3269(9)	6.6(3)
C(264)	-0.4324(7)	0.0568(5)	0.3918(10)	6.9(3)
C(265)	-0.4534(7)	0.1078(6)	0.4893(10)	7.3(3)
C(266)	-0.3925(6)	0.1503(5)	0.5204(8)	5.5(2)

$B_{eq} = 8/3\ \pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha]$

Table 2. Selected Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
Fe(11)	C(131)	2.089(6)	Fe(11)	C(132)	2.041(6)
Fe(11)	C(133)	2.028(7)	Fe(11)	C(134)	2.037(7)
Fe(11)	C(135)	2.056(6)	Fe(11)	C(141)	2.038(9)
Fe(11)	C(142)	2.029(9)	Fe(11)	C(143)	2.016(8)
Fe(11)	C(144)	1.996(8)	Fe(11)	C(145)	2.012(9)
Fe(12)	C(111)	2.086(6)	Fe(12)	C(112)	2.043(6)
Fe(12)	C(113)	2.033(7)	Fe(12)	C(114)	2.030(7)
Fe(12)	C(115)	2.053(7)	Fe(12)	C(121)	2.031(8)
Fe(12)	C(122)	2.030(8)	Fe(12)	C(123)	2.031(8)
Fe(12)	C(124)	2.048(8)	Fe(12)	C(125)	2.037(8)

Table 2. Selected Bond Lengths(Å) (Continued)

Fe(21)	C(211)	2.084(6)	Fe(21)	C(212)	2.044(7)
Fe(21)	C(213)	2.034(7)	Fe(21)	C(214)	2.026(7)
Fe(21)	C(215)	2.049(6)	Fe(21)	C(221)	2.042(8)
Fe(21)	C(222)	2.028(8)	Fe(21)	C(223)	2.026(7)
Fe(21)	C(224)	2.042(8)	Fe(21)	C(225)	2.029(7)
Fe(22)	C(231)	2.082(6)	Fe(22)	C(232)	2.046(6)
Fe(22)	C(233)	2.044(7)	Fe(22)	C(234)	2.052(7)
Fe(22)	C(235)	2.036(7)	Fe(22)	C(241)	2.01(1)
Fe(22)	C(242)	2.01(1)	Fe(22)	C(243)	1.997(9)
Fe(22)	C(244)	2.046(9)	Fe(22)	C(245)	2.013(9)
O(11)	C(11)	1.215(8)	O(12)	C(14)	1.217(7)
O(21)	C(21)	1.212(7)	O(22)	C(24)	1.207(8)
C(11)	C(12)	1.517(9)	C(11)	C(151)	1.500(9)
C(12)	C(13)	1.559(8)	C(12)	C(111)	1.500(8)
C(13)	C(14)	1.517(8)	C(13)	C(131)	1.505(9)
C(14)	C(161)	1.497(9)	C(21)	C(22)	1.512(9)
C(21)	C(251)	1.484(9)	C(22)	C(23)	1.548(8)
C(22)	C(211)	1.487(8)	C(23)	C(24)	1.533(9)
C(23)	C(231)	1.504(9)	C(24)	C(261)	1.498(9)
C(111)	C(112)	1.409(9)	C(111)	C(115)	1.423(8)
C(112)	C(113)	1.440(10)	C(113)	C(114)	1.405(10)
C(114)	C(115)	1.406(10)	C(121)	C(122)	1.37(1)
C(121)	C(125)	1.43(1)	C(122)	C(123)	1.40(1)
C(123)	C(124)	1.39(1)	C(124)	C(125)	1.35(1)
C(131)	C(132)	1.431(8)	C(131)	C(135)	1.416(9)
C(132)	C(133)	1.438(10)	C(133)	C(134)	1.406(10)
C(134)	C(135)	1.395(9)	C(141)	C(142)	1.40(2)
C(141)	C(145)	1.36(2)	C(142)	C(143)	1.32(1)
C(143)	C(144)	1.33(1)	C(144)	C(145)	1.41(1)
C(151)	C(152)	1.376(9)	C(151)	C(156)	1.375(9)
C(152)	C(153)	1.40(1)	C(153)	C(154)	1.36(1)
C(154)	C(155)	1.35(1)	C(155)	C(156)	1.387(10)
C(161)	C(162)	1.396(9)	C(161)	C(166)	1.367(9)
C(162)	C(163)	1.376(10)	C(163)	C(164)	1.36(1)
C(164)	C(165)	1.37(1)	C(165)	C(166)	1.380(10)
C(211)	C(212)	1.427(8)	C(211)	C(215)	1.415(9)
C(212)	C(213)	1.434(9)	C(213)	C(214)	1.396(9)
C(214)	C(215)	1.421(9)	C(221)	C(222)	1.39(1)
C(221)	C(225)	1.42(1)	C(222)	C(223)	1.39(1)
C(223)	C(224)	1.36(1)	C(224)	C(225)	1.38(1)
C(231)	C(232)	1.419(8)	C(231)	C(235)	1.419(9)
C(232)	C(233)	1.397(9)	C(233)	C(234)	1.375(10)
C(234)	C(235)	1.438(10)	C(241)	C(242)	1.30(2)
C(241)	C(245)	1.32(1)	C(242)	C(243)	1.46(2)
C(243)	C(244)	1.35(1)	C(244)	C(245)	1.31(1)
C(251)	C(252)	1.375(9)	C(251)	C(256)	1.373(9)
C(252)	C(253)	1.388(10)	C(253)	C(254)	1.36(1)
C(254)	C(255)	1.36(1)	C(255)	C(256)	1.386(10)
C(261)	C(262)	1.374(9)	C(261)	C(266)	1.380(9)
C(262)	C(263)	1.39(1)	C(263)	C(264)	1.38(1)
C(264)	C(265)	1.37(1)	C(265)	C(266)	1.41(1)

Table 3. Selected Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O(11)	C(11)	C(12)	119.2(6)	O(11)	C(11)	C(151)	121.1(6)
C(12)	C(11)	C(151)	119.7(6)	C(11)	C(12)	C(13)	110.5(5)
C(11)	C(12)	C(111)	111.8(5)	C(13)	C(12)	C(111)	108.9(5)
C(12)	C(13)	C(14)	110.2(5)	C(12)	C(13)	C(131)	108.8(5)
C(14)	C(13)	C(131)	111.7(5)	O(12)	C(14)	C(13)	120.0(6)
O(12)	C(14)	C(161)	120.5(6)	C(13)	C(14)	C(161)	119.5(6)
O(21)	C(21)	C(22)	119.5(6)	O(21)	C(21)	C(251)	120.1(6)
C(22)	C(21)	C(251)	120.2(6)	C(21)	C(22)	C(23)	110.2(5)
C(21)	C(22)	C(211)	110.9(5)	C(23)	C(22)	C(211)	109.0(5)
C(22)	C(23)	C(24)	109.6(5)	C(22)	C(23)	C(231)	109.7(5)
C(24)	C(23)	C(231)	111.7(5)	O(22)	C(24)	C(23)	118.6(6)
O(22)	C(24)	C(261)	121.4(6)	C(23)	C(24)	C(261)	120.0(6)

Table 4. Selected Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(11)	C(11)	C(12)	C(13)	38.0(8)	O(11)	C(11)	C(12)	C(111)	-83.4(8)
O(11)	C(11)	C(151)	C(152)	2(1)	O(11)	C(11)	C(151)	C(156)	-180.0(7)
O(12)	C(14)	C(13)	C(12)	35.1(9)	O(12)	C(14)	C(13)	C(131)	-86.0(8)
O(12)	C(14)	C(161)	C(162)	11(1)	O(12)	C(14)	C(161)	C(166)	-171.5(8)
O(21)	C(21)	C(22)	C(23)	-40.1(9)	O(21)	C(21)	C(22)	C(211)	80.6(8)
O(21)	C(21)	C(251)	C(252)	-26(1)	O(21)	C(21)	C(251)	C(256)	153.3(8)
O(22)	C(24)	C(23)	C(22)	-44.6(9)	O(22)	C(24)	C(23)	C(231)	77.2(8)
O(22)	C(24)	C(261)	C(262)	-10(1)	O(22)	C(24)	C(261)	C(266)	169.5(8)
C(11)	C(12)	C(13)	C(14)	58.4(7)	C(11)	C(12)	C(13)	C(131)	-178.8(5)
C(11)	C(12)	C(111)	C(112)	55.1(8)	C(11)	C(12)	C(111)	C(115)	-137.3(6)
C(12)	C(11)	C(151)	C(152)	-177.5(6)	C(12)	C(11)	C(151)	C(156)	0(1)
C(12)	C(13)	C(14)	C(161)	-147.9(6)	C(12)	C(13)	C(131)	C(132)	-65.7(8)
C(12)	C(13)	C(131)	C(135)	102.2(7)	C(13)	C(12)	C(11)	C(151)	-141.8(6)
C(13)	C(12)	C(111)	C(112)	-67.2(8)	C(13)	C(12)	C(111)	C(115)	100.3(7)
C(13)	C(14)	C(161)	C(162)	-165.3(8)	C(13)	C(14)	C(161)	C(166)	11(1)
C(14)	C(13)	C(12)	C(111)	-178.5(5)	C(14)	C(13)	C(131)	C(132)	56.2(8)
C(14)	C(13)	C(131)	C(135)	-135.9(6)	C(21)	C(22)	C(23)	C(24)	-59.7(7)
C(21)	C(22)	C(23)	C(231)	177.3(5)	C(21)	C(22)	C(211)	C(212)	-43.0(8)
C(21)	C(22)	C(211)	C(215)	149.2(6)	C(22)	C(21)	C(251)	C(252)	149.7(7)
C(22)	C(21)	C(251)	C(256)	-30(1)	C(22)	C(23)	C(24)	C(261)	135.9(6)
C(22)	C(23)	C(231)	C(232)	-94.7(7)	C(22)	C(23)	C(231)	C(235)	75.3(8)
C(23)	C(22)	C(21)	C(251)	143.5(6)	C(23)	C(22)	C(211)	C(212)	78.5(8)
C(23)	C(22)	C(211)	C(215)	-89.3(7)	C(23)	C(24)	C(261)	C(262)	168.6(7)
C(23)	C(24)	C(261)	C(266)	-11(1)	C(24)	C(23)	C(22)	C(211)	178.4(5)
C(24)	C(23)	C(231)	C(232)	143.6(6)	C(24)	C(23)	C(231)	C(235)	-46.4(9)
C(111)	C(12)	C(11)	C(151)	96.7(7)	C(111)	C(12)	C(13)	C(131)	-55.6(6)
C(131)	C(13)	C(14)	C(161)	91.0(7)	C(211)	C(22)	C(21)	C(251)	-95.8(7)
C(211)	C(22)	C(23)	C(231)	55.5(7)	C(231)	C(23)	C(24)	C(261)	-102.3(7)

APPENDIX VI*

Crystallographic data for *racemic* 2,3-diferrocenyl-1,4-bis(biphenyl)butane-1,4-dione (42b)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{48}H_{38}Fe_2O_2$
Formula Weight	758.52
Crystal Colour, Habit	orange, block
Crystal Dimensions	0.50 X 0.30 X 0.25 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (24.5 - 25.0°)
Omega Scan Peak Width at Half-height	0.28°
Lattice Parameters	a = 12.617(5)Å b = 13.464(4) Å c = 11.870(3) Å α = 98.91(3)° β = 105.27(2)° γ = 104.88(3)° V = 1825(1) Å^3
Space Group	$P\bar{1}$ (No. 2)
Z value	2
D_{calc}	1.380 g/cm^3
F_{000}	788.00
$\mu(M_o K_\alpha)$	8.32 cm^{-1}

* Following the university restriction for the size of thesis only selected data are presented here, for the detailed account of atomic coordinates, geometric parameters and anisotropic factors pleases refer to **Cambridge Crystallographic Database** ref. *J. Organomet. Chem.*, 1997, **542**, 81.

B. Intensity Measurements

Diffractometer	Rigaku AFC7S
Radiation	M_o K_α (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 8.53)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	235 mm
Temperature	20.0 °C
Scan Type	ω-2θ
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	(1.84 + 0.35 tan θ)°
$2\theta_{max}$	50.0°
No. of Reflections Measured	Total: 6706 Unique: 6391 (R_{int} = 0.021)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\omega$ (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2$ (Fo) = $4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0020
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	4599
No. Variables	469
Reflection/Parameter Ratio	9.81
Residuals: R; Rw	0.040 ; 0.034
Goodness of Fit Indicator	2.34
Max Shift/Error in Final Cycle	0.13
Maximum peak in Final Diff. Map	0.40 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.48 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe(1)	0.93855(4)	0.54355(4)	0.21572(5)	4.07(1)
Fe(2)	0.78740(5)	-0.00855(4)	0.07288(5)	4.93(1)
O(1)	0.7856(2)	0.3626(2)	0.4282(2)	4.76(6)
O(2)	0.5808(2)	0.1596(2)	0.2391(2)	5.01(7)
C(1)	0.7373(3)	0.3688(2)	0.3275(3)	3.53(8)
C(2)	0.7662(3)	0.3164(2)	0.2214(3)	3.18(7)
C(3)	0.7750(3)	0.2058(2)	0.2361(3)	3.19(7)
C(4)	0.6760(3)	0.1501(2)	0.2788(3)	3.67(8)
C(11)	0.8793(3)	0.3856(2)	0.2161(3)	3.28(7)
C(12)	0.9097(3)	0.3987(2)	0.1112(3)	4.11(8)
C(13)	1.0279(3)	0.4587(3)	0.1470(4)	4.72(10)
C(14)	1.0705(3)	0.4848(3)	0.2728(4)	4.92(10)
C(15)	0.9799(3)	0.4408(3)	0.3168(3)	4.28(9)
C(21)	0.8160(4)	0.6194(3)	0.2106(6)	7.0(1)
C(22)	0.8608(5)	0.6304(3)	0.1150(5)	7.4(2)
C(23)	0.9791(5)	0.6819(3)	0.1637(5)	7.1(2)
C(24)	1.0093(4)	0.7018(3)	0.2876(5)	7.3(1)
C(25)	0.9082(5)	0.6624(3)	0.3181(5)	7.6(2)
C(31)	0.7675(3)	0.1382(2)	0.1184(3)	3.52(8)
C(32)	0.6654(3)	0.0650(3)	0.0321(4)	5.25(10)
C(33)	0.6924(4)	0.0272(3)	-0.0706(4)	6.0(1)
C(34)	0.8086(4)	0.0747(3)	-0.0510(4)	5.6(1)
C(35)	0.8570(3)	0.1438(3)	0.0660(3)	4.94(10)
C(41)	0.8439(9)	-0.0637(6)	0.2181(6)	11.9(3)
C(42)	0.7353(8)	-0.1275(5)	0.1534(9)	12.1(3)
C(43)	0.7405(7)	-0.1694(4)	0.0372(6)	10.4(2)
C(44)	0.8512(7)	-0.1282(5)	0.0351(5)	9.5(2)
C(45)	0.9199(5)	-0.0619(4)	0.1495(6)	10.1(2)
C(51)	0.6541(3)	0.4305(2)	0.3086(3)	3.34(7)
C(52)	0.5704(3)	0.4167(2)	0.1996(3)	3.89(8)
C(53)	0.4980(3)	0.4791(3)	0.1880(3)	4.12(8)
C(54)	0.5079(3)	0.5575(2)	0.2851(3)	3.63(8)
C(55)	0.5898(3)	0.5695(3)	0.3943(3)	4.35(9)
C(56)	0.6619(3)	0.5075(3)	0.4065(3)	4.18(9)
C(61)	0.4351(3)	0.6288(2)	0.2735(3)	3.90(8)
C(62)	0.4140(3)	0.6721(3)	0.1747(3)	5.0(1)
C(63)	0.3528(3)	0.7443(3)	0.1681(4)	5.7(1)
C(64)	0.3113(3)	0.7726(3)	0.2592(4)	5.5(1)
C(65)	0.3301(3)	0.7298(3)	0.3571(4)	5.2(1)
C(66)	0.3921(3)	0.6585(3)	0.3648(3)	4.50(9)
C(71)	0.6963(3)	0.0822(2)	0.3648(3)	3.48(8)
C(72)	0.6020(3)	0.0005(3)	0.3631(3)	4.63(9)
C(73)	0.6166(3)	-0.0678(3)	0.4376(3)	4.94(10)
C(74)	0.7235(3)	-0.0563(2)	0.5169(3)	3.83(8)
C(75)	0.8166(3)	0.0288(3)	0.5224(3)	4.10(8)
C(76)	0.8030(3)	0.0962(2)	0.4466(3)	3.98(8)
C(81)	0.7376(3)	-0.1344(2)	0.5905(3)	4.04(8)
C(82)	0.6546(3)	-0.1761(3)	0.6412(3)	4.83(10)
C(83)	0.6653(4)	-0.2533(3)	0.7041(3)	6.1(1)
C(84)	0.7579(4)	-0.2903(3)	0.7164(4)	6.4(1)
C(85)	0.8412(4)	-0.2496(3)	0.6677(4)	6.1(1)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (Continued)

atom	x	y	z	B_{eq}
C(86)	0.8315(3)	-0.1726(3)	0.6040(3)	5.07(10)
Fe(1*)	0.06145(4)	0.45645(4)	0.78428(5)	4.07(1)
Fe(2*)	0.21260(5)	1.00855(4)	0.92712(5)	4.93(1)
O(1*)	0.2144(2)	0.6374(2)	0.5718(2)	4.76(6)
O(2*)	0.4192(2)	0.8404(2)	0.7609(2)	5.01(7)
C(1*)	0.2627(3)	0.6312(2)	0.6725(3)	3.53(8)
C(2*)	0.2338(3)	0.6836(2)	0.7786(3)	3.18(7)
C(3*)	0.2250(3)	0.7942(2)	0.7639(3)	3.19(7)
C(4*)	0.3240(3)	0.8499(2)	0.7212(3)	3.67(8)
C(11*)	0.1207(3)	0.6144(2)	0.7839(3)	3.28(7)
C(12*)	0.0903(3)	0.6013(2)	0.8888(3)	4.11(8)
C(13*)	-0.0279(3)	0.5413(3)	0.8530(4)	4.72(10)
C(14*)	-0.0705(3)	0.5152(3)	0.7272(4)	4.92(10)
C(15*)	0.0201(3)	0.5592(3)	0.6832(3)	4.28(9)
C(21*)	0.1840(4)	0.3806(3)	0.7894(6)	7.0(1)
C(22*)	0.1392(5)	0.3696(3)	0.8850(5)	7.4(2)
C(23*)	0.0209(5)	0.3181(3)	0.8363(5)	7.1(2)
C(24*)	-0.0093(4)	0.2982(3)	0.7124(5)	7.3(1)
C(25*)	0.0918(5)	0.3376(3)	0.6819(5)	7.6(2)
C(31*)	0.2325(3)	0.8618(2)	0.8816(3)	3.52(8)
C(32*)	0.3346(3)	0.9350(3)	0.9679(4)	5.25(10)
C(33*)	0.3076(4)	0.9728(3)	1.0706(4)	6.0(1)
C(34*)	0.1914(4)	0.9253(3)	1.0510(4)	5.6(1)
C(35*)	0.1430(3)	0.8562(3)	0.9340(3)	4.94(10)
C(41*)	0.1561(9)	1.0637(6)	0.7819(6)	11.9(3)
C(42*)	0.2647(8)	1.1275(5)	0.8466(9)	12.1(3)
C(43*)	0.2595(7)	1.1694(4)	0.9628(6)	10.4(2)
C(44*)	0.1488(7)	1.1282(5)	0.9649(5)	9.5(2)
C(45*)	0.0801(5)	1.0619(4)	0.8505(6)	10.1(2)
C(51*)	0.3459(3)	0.5695(2)	0.6914(3)	3.34(7)
C(52*)	0.4296(3)	0.5833(2)	0.8004(3)	3.89(8)
C(53*)	0.5020(3)	0.5209(3)	0.8120(3)	4.12(8)
C(54*)	0.4921(3)	0.4425(2)	0.7149(3)	3.63(8)
C(55*)	0.4102(3)	0.4305(3)	0.6057(3)	4.35(9)
C(56*)	0.3381(3)	0.4925(3)	0.5935(3)	4.18(9)
C(61*)	0.5649(3)	0.3712(2)	0.7265(3)	3.90(8)
C(62*)	0.5860(3)	0.3279(3)	0.8253(3)	5.0(1)
C(63*)	0.6472(3)	0.2557(3)	0.8319(4)	5.7(1)
C(64*)	0.6887(3)	0.2274(3)	0.7408(4)	5.5(1)
C(65*)	0.6699(3)	0.2702(3)	0.6429(4)	5.2(1)
C(66*)	0.6079(3)	0.3415(3)	0.6352(3)	4.50(9)
C(71*)	0.3037(3)	0.9178(2)	0.6352(3)	3.48(8)
C(72*)	0.3980(3)	0.9995(3)	0.6369(3)	4.63(9)
C(73*)	0.3834(3)	1.0678(3)	0.5624(3)	4.94(10)
C(74*)	0.2765(3)	1.0563(2)	0.4831(3)	3.83(8)
C(75*)	0.1834(3)	0.9712(3)	0.4776(3)	4.10(8)
C(76*)	0.1970(3)	0.9038(2)	0.5534(3)	3.98(8)
C(81*)	0.2624(3)	1.1344(2)	0.4095(3)	4.04(8)
C(82*)	0.3454(3)	1.1761(3)	0.3588(3)	4.83(10)
C(83*)	0.3347(4)	1.2533(3)	0.2959(3)	6.1(1)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (Continued)

atom	x	y	z	B_{eq}
C(84*)	0.2421(4)	1.2903(3)	0.2836(4)	6.4(1)
C(85*)	0.1588(4)	1.2496(3)	0.3323(4)	6.1(1)
C(86*)	0.1685(3)	1.1726(3)	0.3960(3)	5.07(10)

$$B_{eq} = 8/3\ \pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha]$$

Table 2. Selected Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	C(1)	1.217(3)	O(2)	C(4)	1.217(4)
C(1)	C(2)	1.522(4)	C(1)	C(51)	1.491(4)
C(2)	C(3)	1.554(4)	C(2)	C(11)	1.513(4)
C(3)	C(4)	1.533(4)	C(3)	C(31)	1.511(4)
C(4)	C(71)	1.488(4)			

Table 3. Selected Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	C(1)	C(2)	119.3(3)	O(1)	C(1)	C(51)	120.4(3)
C(2)	C(1)	C(51)	120.3(3)	C(1)	C(2)	C(3)	109.2(2)
C(1)	C(2)	C(11)	109.5(2)	C(3)	C(2)	C(11)	110.5(2)
C(2)	C(3)	C(4)	109.4(2)	C(2)	C(3)	C(31)	110.9(2)
C(4)	C(3)	C(31)	109.0(2)	O(2)	C(4)	C(3)	119.4(3)
O(2)	C(4)	C(71)	120.8(3)	C(3)	C(4)	C(71)	119.8(3)
C(2)	C(11)	C(12)	126.9(3)	C(2)	C(11)	C(15)	125.7(3)
C(3)	C(31)	C(32)	126.2(3)	C(3)	C(31)	C(35)	127.0(3)
C(4)	C(71)	C(72)	117.8(3)	C(4)	C(71)	C(76)	123.8(3)

Table 4. Selected Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	C(1)	C(2)	C(3)	42.1(4)	O(1)	C(1)	C(2)	C(11)	-79.0(4)
O(1)	C(1)	C(51)	C(52)	-159.5(3)	O(1)	C(1)	C(51)	C(56)	21.2(5)
O(2)	C(4)	C(3)	C(2)	38.2(4)	O(2)	C(4)	C(3)	C(31)	-83.2(3)
O(2)	C(4)	C(71)	C(72)	24.8(5)	O(2)	C(4)	C(71)	C(76)	-154.9(3)
C(1)	C(2)	C(3)	C(4)	42.6(3)	C(1)	C(2)	C(3)	C(31)	162.9(2)
C(1)	C(2)	C(11)	C(12)	-146.0(3)	C(1)	C(2)	C(11)	C(15)	41.4(4)
C(2)	C(1)	C(51)	C(52)	22.8(5)	C(2)	C(1)	C(51)	C(56)	-156.5(3)
C(2)	C(3)	C(4)	C(71)	-143.8(3)	C(2)	C(3)	C(31)	C(32)	-93.3(4)
C(2)	C(3)	C(31)	C(35)	78.9(4)	C(3)	C(2)	C(1)	C(51)	-140.2(3)
C(3)	C(2)	C(11)	C(12)	93.6(4)	C(3)	C(2)	C(11)	C(15)	-79.0(4)
C(3)	C(4)	C(71)	C(72)	-153.2(3)	C(3)	C(4)	C(71)	C(76)	27.1(5)
C(4)	C(3)	C(2)	C(11)	163.1(2)	C(4)	C(3)	C(31)	C(32)	27.2(4)
C(4)	C(3)	C(31)	C(35)	-160.6(3)	C(11)	C(2)	C(1)	C(51)	98.7(3)
C(11)	C(2)	C(3)	C(31)	-76.6(3)	C(31)	C(3)	C(4)	C(71)	94.8(3)

APPENDIX VII*

Crystallographic data for *meso*-2,3-diferrocenyl-1,4-bis(biphenyl)butane-1,4-dione (42b)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{48}H_{38}Fe_2O_2$
Formula Weight	758.52
Crystal Colour, Habit	orange, needle
Crystal Dimensions	0.10 X 0.05 X 0.45 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit Cell Determination (2θ range)	13 (6.8 - 11.7°)
Omega Scan Peak Width at Half-height	0.30°
Lattice Parameters	a = 6.034(4)Å b = 28.68(3) Å c = 21.612(7) Å β = 90.14(6)° V = 3740(3) Å^3
Space Group	Cc (No. 9)
Z value	4
D_{calc}	1.347 g/cm^3
F(000)	1576.00
$\mu(M_o K_\alpha)$	8.14 cm^{-1}

* Following the university restriction for the size of thesis only selected data are presented here, for the detailed account of atomic coordinates, geometric parameters and anisotropic factors pleases refer to **Cambridge Crystallographic Database** ref. *J. Organomet. Chem.*, 1997, **542**, 81.

B. Intensity Measurements

Diffractometer	Rigaku AFC7S
Radiation	$M_o K_\alpha$ (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 8.53)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal 13.0 mm vertical
Crystal to Detector Distance	235 mm
Temperature	20.0 °C
Scan Type	ω-2θ
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	(0.89 + 0.35 tan θ)°
$2\theta_{max}$	47.0°
No. of Reflections Measured	Total: 3136 Unique: 2829 (R_{int} = 0.048)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\ \omega\ (|Fo| - |Fc|)^2$
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0000
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00sigma(I))	1682
No. Variables	227
Reflection/Parameter Ratio	7.41
Residuals: R; Rw	0.070 ; 0.060
Goodness of Fit Indicator	2.43
Max Shift/Error in Final Cycle	0.09
Maximum peak in Final Diff. Map	0.92 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.40 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe(1)	0.1724	0.14577(9)	0.8419	3.00(7)
Fe(2)	0.4415(6)	0.16587(9)	0.4925(2)	3.28(8)
O(1)	0.659(2)	0.1906(4)	0.7153(7)	3.7(4)
O(2)	-0.031(2)	0.1168(4)	0.6198(6)	2.8(3)
C(1)	0.461(3)	0.2036(6)	0.7132(8)	2.0(4)
C(2)	0.280(3)	0.1683(6)	0.6988(9)	2.3(4)
C(3)	0.339(3)	0.1421(6)	0.6370(9)	2.5(4)
C(4)	0.158(3)	0.1046(7)	0.6228(8)	2.6(4)
C(11)	0.263(4)	0.1316(7)	0.7521(9)	2.8(4)
C(12)	0.433(3)	0.1181(7)	0.7922(9)	3.4(4)
C(13)	0.344(4)	0.0855(7)	0.832(1)	4.4(5)
C(14)	0.109(4)	0.0788(7)	0.8175(9)	4.0(5)
C(15)	0.058(3)	0.1098(7)	0.7668(9)	3.4(4)
C(21)	0.116(4)	0.2150(7)	0.8586(10)	4.2(5)
C(22)	0.283(4)	0.1915(9)	0.906(1)	5.6(6)
C(23)	0.116(4)	0.1572(7)	0.9330(10)	4.0(5)
C(24)	-0.069(6)	0.164(1)	0.900(2)	9.2(9)
C(25)	-0.071(4)	0.1934(9)	0.861(1)	6.0(6)
C(31)	0.356(3)	0.1751(6)	0.5844(8)	1.9(4)
C(32)	0.179(3)	0.1927(7)	0.5428(9)	3.4(4)
C(33)	0.281(4)	0.2280(7)	0.5039(10)	4.1(5)
C(34)	0.513(4)	0.2324(8)	0.521(1)	4.8(5)
C(35)	0.551(4)	0.2013(8)	0.5686(10)	3.6(5)
C(41)	0.434(4)	0.0979(8)	0.467(1)	5.2(6)
C(42)	0.315(5)	0.123(1)	0.427(1)	7.7(8)
C(43)	0.430(4)	0.1545(8)	0.401(1)	5.6(6)
C(44)	0.663(4)	0.1523(7)	0.424(1)	4.6(5)
C(45)	0.674(5)	0.1167(9)	0.469(1)	6.2(6)
C(51)	0.408(3)	0.2529(6)	0.7242(8)	2.1(4)
C(52)	0.578(4)	0.2815(8)	0.7500(10)	4.0(5)
C(53)	0.529(4)	0.3271(8)	0.759(1)	4.0(5)
C(54)	0.327(3)	0.3489(6)	0.7449(8)	2.8(4)
C(55)	0.164(3)	0.3200(7)	0.7207(9)	3.4(5)
C(56)	0.194(3)	0.2729(6)	0.7103(9)	2.9(4)
C(61)	0.280(3)	0.4007(6)	0.7533(9)	3.2(4)
C(62)	0.458(3)	0.4310(7)	0.7402(9)	3.4(4)
C(63)	0.411(4)	0.4797(8)	0.747(1)	4.7(5)
C(64)	0.221(4)	0.4946(7)	0.767(1)	4.0(5)
C(65)	0.043(4)	0.4659(9)	0.783(1)	5.3(6)
C(66)	0.090(3)	0.4171(7)	0.7755(9)	3.3(4)
C(71)	0.224(3)	0.0547(6)	0.6106(8)	1.9(4)
C(72)	0.067(3)	0.0270(7)	0.5857(8)	2.8(4)
C(73)	0.109(3)	-0.0204(7)	0.5766(9)	3.4(5)
C(74)	0.307(3)	-0.0402(6)	0.5942(8)	2.6(4)
C(75)	0.477(4)	-0.0127(7)	0.620(1)	3.3(5)
C(76)	0.417(3)	0.0345(7)	0.6283(9)	3.5(4)
C(81)	0.346(3)	-0.0913(6)	0.5860(8)	2.5(4)
C(82)	0.189(3)	-0.1237(6)	0.6020(9)	2.9(4)
C(83)	0.224(3)	-0.1713(7)	0.5960(9)	3.3(4)
C(84)	0.421(4)	-0.1869(7)	0.5757(9)	4.0(5)

C(85)	0.583(3)	-0.1559(7)	0.5600(9)	2.9(5)
C(86)	0.553(4)	-0.1077(8)	0.567(1)	4.2(5)

$$B_{eq} = 8/3\ \pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha]$$

Table 2. Selected Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	C(1)	1.26(2)	O(2)	C(4)	1.19(2)
C(1)	C(2)	1.52(2)	C(1)	C(51)	1.47(2)
C(2)	C(3)	1.58(2)	C(2)	C(11)	1.56(3)
C(3)	C(4)	1.57(2)	C(3)	C(31)	1.48(2)
C(4)	C(71)	1.51(3)			

Table 3. Selected Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	C(1)	C(2)	119(1)	O(1)	C(1)	C(51)	119(1)
C(2)	C(1)	C(51)	121(1)	C(1)	C(2)	C(3)	109(1)
C(1)	C(2)	C(11)	110(1)	C(3)	C(2)	C(11)	108(1)
C(2)	C(3)	C(4)	109(1)	C(2)	C(3)	C(31)	111(1)
C(4)	C(3)	C(31)	109(1)	O(2)	C(4)	C(3)	118(1)
O(2)	C(4)	C(71)	121(1)	C(3)	C(4)	C(71)	120(1)
C(2)	C(11)	C(12)	126(1)	C(2)	C(11)	C(15)	121(1)
C(3)	C(31)	C(32)	129(1)	C(3)	C(31)	C(35)	124(1)
C(1)	C(51)	C(52)	117(1)	C(1)	C(51)	C(56)	122(1)
C(4)	C(71)	C(72)	116(1)	C(4)	C(71)	C(76)	125(1)

Table 4. Selected Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	C(1)	C(2)	C(3)	-53(1)	O(1)	C(1)	C(2)	C(11)	65(2)
O(1)	C(1)	C(51)	C(52)	-13(2)	O(1)	C(1)	C(51)	C(56)	166(1)
O(2)	C(4)	C(3)	C(2)	55(2)	O(2)	C(4)	C(3)	C(31)	-66(2)
O(2)	C(4)	C(71)	C(72)	11(2)	O(2)	C(4)	C(71)	C(76)	-161(1)
C(1)	C(2)	C(3)	C(4)	178(1)	C(1)	C(2)	C(3)	C(31)	-60(1)
C(1)	C(2)	C(11)	C(12)	-26(2)	C(1)	C(2)	C(11)	C(15)	149(1)
C(2)	C(1)	C(51)	C(52)	166(1)	C(2)	C(1)	C(51)	C(56)	-12(2)
C(2)	C(3)	C(4)	C(71)	-127(1)	C(2)	C(3)	C(31)	C(32)	-86(2)
C(2)	C(3)	C(31)	C(35)	85(2)	C(3)	C(2)	C(1)	C(51)	126(1)
C(3)	C(2)	C(11)	C(12)	92(2)	C(3)	C(2)	C(11)	C(15)	-91(1)
C(3)	C(4)	C(71)	C(72)	-165(1)	C(3)	C(4)	C(71)	C(76)	21(2)
C(4)	C(3)	C(2)	C(11)	58(1)	C(4)	C(3)	C(31)	C(32)	34(2)
C(4)	C(3)	C(31)	C(35)	-153(1)	C(11)	C(2)	C(1)	C(51)	-114(1)
C(11)	C(2)	C(3)	C(31)	179(1)	C(31)	C(3)	C(4)	C(71)	110(1)

APPENDIX VIII*

Crystallographic data for 3-ferrocenyl-2-phenyl-6-nitro-quinoxaline (53)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{24}H_{17}FeN_3O_2$
Formula Weight	435.26
Crystal Colour, Habit	red, block shape
Crystal Dimensions	0.42 X 0.41 X 0.31 mm
Crystal System	triclinic
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (9.40 - 17.76°)
Omega Scan Peak Width at Half-height	
Lattice Parameters	a = 8.3220(7) Å b = 12.5682(11) Å c = 18.6853(18) Å α = 94.663(8)° β = 96.980(7)° γ = 95.479(6)° V = 1922.4(3) Å^3
Space Group	$P\bar{1}$
Z value	4
D_m	Not measured
D_x	1.504 Mg m^{-3}
F(000)	896
$\mu(M_o K_\alpha)$	0.812 mm^{-1}

* Following the university restriction for the size of thesis only selected data are presented here, for the detailed account of atomic coordinates, geometric parameters and anisotropic factors pleases refer to **Cambridge Crystallographic Database** ref. *Acta Crystallogr. C*, 1998, **54**, in press.

B. Intensity Measurements

Diffractometer	Enraf-Nonius CAD-4
Radiation	$M_o K_\alpha$ ($\lambda = 0.7107$ Å) graphite monochromated
Temperature	294 (1) K
Scan Type	$\theta/2\theta$
θ_{max}	25.36°
	h = -10 to 9
	k = 0 to 15
	l = -22 to 22
No. of Reflections Measured	Total: 7076
	Observed: 5046
Absorption Correction	Gaussian ABSO in NRCVAX
3 standard reflections	frequency: 240 min
	intensity decay: 1.7%
R_{int}	0.013

C. Structure Solution and Refinement

Structure Solution	Patterson heavy-atom method and difmap
Extinction correction	none
Refinement on F^2	$R[F^2 > 2\sigma(F^2)] = 0.0407$
	$\omega R(F^2) = 0.1109$
	S = 0.951
Number of Reflections	7076
Number of parameters	575
H atom parameters	constrained

$w = 1/[\sigma^2 (F_o^2) + (0.0597\ P)^2 + 0.7344\ P]$ where $P = (Fo^2 + 2Fc^2)/3$

Max Shift/Error in Final Cycle $(\Delta/\sigma)_{max}$	0.001
Maximum peak in Final Diff. Map (ΔP_{max})	0.225 $e^-/Å^3$
Minimum peak in Final Diff. Map (ΔP_{min})	-0.303 $e^-/Å^3$

Table 1. Fractional Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for I

atom	Occupancy	x	y	z	U_{eq}
Fe1	1	0.09262(5)	0.89311(3)	0.87066(2)	0.04842(13)
N1	0.813(3)	0.5344(5)	0.6326(3)	0.83218(19)	0.0583(9)
C2	0.813(3)	0.4533(5)	0.7155(3)	0.8227(2)	0.0468(10)
C3	0.813(3)	0.4247(5)	0.7898(3)	0.88180(19)	0.0450(9)
N4	0.813(3)	0.4796(5)	0.7743(3)	0.94912(17)	0.0508(8)
C5	0.813(3)	0.5645(5)	0.6864(4)	0.9587(2)	0.0514(9)
C6	0.813(3)	0.6204(5)	0.6679(3)	1.0302(2)	0.0573(10)
C7	0.813(3)	0.7064(5)	0.5814(3)	1.04140(17)	0.0547(10)
C8	0.813(3)	0.7397(5)	0.5126(3)	0.9838(2)	0.0676(12)
C9	0.813(3)	0.6849(6)	0.5301(4)	0.9150(2)	0.0691(12)
C10	0.813(3)	0.5946(5)	0.6172(3)	0.9013(2)	0.0544(10)
N1A	0.187(3)	0.5473(19)	0.6339(11)	0.8460(4)	0.055(3)
C2A	0.187(3)	0.462(2)	0.7109(12)	0.8247(4)	0.055(3)
C3A	0.187(3)	0.415(2)	0.7913(11)	0.8755(5)	0.055(3)
N4A	0.187(3)	0.4614(19)	0.7903(10)	0.9459(5)	0.055(3)
C5A	0.187(3)	0.5506(12)	0.7115(7)	0.9684(4)	0.055(3)
C6A	0.187(3)	0.6038(15)	0.7086(8)	1.0430(4)	0.055(3)
C7A	0.187(3)	0.6925(14)	0.6290(8)	1.0656(4)	0.055(3)
C8A	0.187(3)	0.7310(14)	0.5494(8)	1.0162(4)	0.055(3)
C9A	0.187(3)	0.6822(16)	0.5495(8)	0.9436(4)	0.055(3)
C10A	0.187(3)	0.5931(12)	0.6319(7)	0.9184(4)	0.055(3)
N7	0.813(3)	0.7640(4)	0.5595(3)	1.11708(17)	0.0743(11)
O1	0.813(3)	0.8331(5)	0.4810(3)	1.1242(2)	0.1064(15)
O2	0.813(3)	0.7328(5)	0.6210(3)	1.16445(16)	0.1065(13)
N8A	0.187(3)	0.8441(15)	0.4686(9)	1.0432(5)	0.080
O1A	0.187(3)	0.896(2)	0.4866(14)	1.1062(6)	0.100
O2A	0.187(3)	0.8799(17)	0.4104(10)	0.9945(7)	0.100
C11	1	0.3944(3)	0.7221(2)	0.74539(14)	0.0483(7)
C12	1	0.2485(4)	0.6670(3)	0.71433(17)	0.0612(8)
C13	1	0.1934(4)	0.6714(3)	0.64179(19)	0.0707(9)
C14	1	0.2856(4)	0.7304(3)	0.59984(17)	0.0673(9)
C15	1	0.4321(4)	0.7844(3)	0.62992(17)	0.0653(9)
C16	1	0.4865(4)	0.7811(3)	0.70213(16)	0.0588(8)
C21	1	0.3365(3)	0.8854(2)	0.87090(15)	0.0483(7)
C22	1	0.2652(4)	0.9268(2)	0.80630(16)	0.0536(7)
C23	1	0.1970(4)	1.0212(3)	0.82681(19)	0.0640(9)
C24	1	0.2209(4)	1.0388(3)	0.90263(19)	0.0639(9)
C25	1	0.3064(4)	0.9565(2)	0.92991(17)	0.0573(8)
C31	1	-0.0246(5)	0.7453(3)	0.8739(3)	0.0945(15)
C32	1	-0.0825(5)	0.7900(4)	0.8111(3)	0.0880(12)
C33	1	-0.1462(4)	0.8837(3)	0.8314(2)	0.0785(11)
C34	1	-0.1276(4)	0.8996(3)	0.9068(2)	0.0737(10)
C35	1	-0.0527(5)	0.8141(4)	0.9334(2)	0.0856(12)

Table 1. Fractional Atomic coordinates and equivalent isotropic displacement parameters (Å^2) (continued)

atom	Occupancy	x	y	z	U_{eq}
Fe2	1	0.34772(6)	0.58395(3)	0.36300(2)	0.05476(14)
N41	0.860(3)	0.2062(5)	0.9800(3)	0.33354(18)	0.0586(9)
C42	0.860(3)	0.2753(5)	0.8915(3)	0.32265(19)	0.0512(10)
C43	0.860(3)	0.3492(5)	0.8363(3)	0.38164(18)	0.0486(9)
N44	0.860(3)	0.3459(5)	0.8750(3)	0.44917(16)	0.0534(8)
C45	0.860(3)	0.2694(4)	0.9667(3)	0.46006(19)	0.0497(9)
C46	0.860(3)	0.2604(5)	1.0058(3)	0.53100(18)	0.0534(9)
C47	0.860(3)	0.1851(4)	1.0969(3)	0.54380(15)	0.0490(8)
C48	0.860(3)	0.1197(5)	1.1522(3)	0.48677(19)	0.0653(10)
C49	0.860(3)	0.1294(5)	1.1142(3)	0.4174(2)	0.0676(11)
C50	0.860(3)	0.2027(5)	1.0197(3)	0.4026(2)	0.0539(9)
N41A	0.140(3)	0.203(2)	0.9833(12)	0.3487(4)	0.065(4)
C42A	0.140(3)	0.269(3)	0.8976(13)	0.3260(5)	0.065(4)
C43A	0.140(3)	0.354(3)	0.8337(12)	0.3757(6)	0.065(4)
N44A	0.140(3)	0.366(2)	0.8595(12)	0.4465(5)	0.065(4)
C45A	0.140(3)	0.2981(15)	0.9474(9)	0.4704(4)	0.065(4)
C46A	0.140(3)	0.307(2)	0.9766(11)	0.5456(4)	0.065(4)
C47A	0.140(3)	0.2394(19)	1.0654(10)	0.5696(4)	0.065(4)
C48A	0.140(3)	0.163(2)	1.1288(9)	0.5211(5)	0.065(4)
C49A	0.140(3)	0.152(2)	1.1032(10)	0.4479(5)	0.065(4)
C50A	0.140(3)	0.2173(16)	1.0108(9)	0.4214(4)	0.065(4)
N47	0.860(3)	0.1694(4)	1.1354(2)	0.61968(15)	0.0646(9)
O3	0.860(3)	0.0855(7)	1.2068(4)	0.62839(18)	0.0865(12)
O4	0.860(3)	0.2404(4)	1.0917(3)	0.66656(14)	0.0895(10)
N48A	0.140(3)	0.083(2)	1.2245(10)	0.5505(7)	0.080
O3A	0.140(3)	0.059(5)	1.221(2)	0.6123(10)	0.100
O4A	0.140(3)	0.053(2)	1.2859(11)	0.5060(9)	0.100
C51	1	0.2656(4)	0.8531(2)	0.24559(15)	0.0508(7)
C52	1	0.1368(4)	0.7827(3)	0.21120(18)	0.0672(9)
C53	1	0.1290(5)	0.7507(3)	0.13834(19)	0.0816(11)
C54	1	0.2475(4)	0.7877(3)	0.09915(19)	0.0725(10)
C55	1	0.3748(5)	0.8587(3)	0.13285(18)	0.0720(10)
C56	1	0.3841(4)	0.8911(3)	0.20554(18)	0.0645(9)
C61	1	0.4384(4)	0.7417(2)	0.37034(15)	0.0523(7)
C62	1	0.4734(4)	0.6851(3)	0.30482(18)	0.0605(8)
C63	1	0.5677(4)	0.6020(3)	0.3244(2)	0.0708(9)
C64	1	0.5893(4)	0.6045(3)	0.4002(2)	0.0725(10)
C65	1	0.5112(4)	0.6896(3)	0.42887(17)	0.0612(8)
C71	1	0.1026(5)	0.5677(3)	0.3633(3)	0.0904(13)
C72	1	0.1417(5)	0.5163(4)	0.2997(2)	0.0864(12)
C73	1	0.2410(5)	0.4382(3)	0.3186(2)	0.0865(12)
C74	1	0.2639(5)	0.4395(3)	0.3929(2)	0.0844(11)
C75	1	0.1794(5)	0.5195(3)	0.4216(2)	0.0838(11)

$$U_{eq} = (1/3)\ \Sigma_i\ \Sigma_j\ U_{ij}\ a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$$

Table 2. Selected Bond Lengths (Å) for I

atom	atom	distance	atom	atom	distance
N1	C2	1.308(4)	N1	C10	1.362(5)
C2	C3	1.444(5)	C3	N4	1.321(4)
N4	C5	1.379(5)	C5	C10	1.388(5)
C5	C6	1.406(5)	C6	C7	1.374(5)
C7	C8	1.396(5)	C8	C9	1.353(5)
C9	C10	1.408(5)	C7	N7	1.493(4)
N7	O1	1.197(3)	N7	O2	1.197(3)
C2	C11	1.479(4)	C3	C21	1.483(4)
N41	C42	1.312(4)	N41	C50	1.350(4)
C42	C43	1.454(5)	C43	N44	1.319(4)
N44	C45	1.382(4)	C45	C46	1.389(4)
C45	C50	1.395(5)	C46	C47	1.375(4)
C47	C48	1.402(5)	C48	C49	1.360(5)
C49	C50	1.409(5) .	C47	N47	1.486(3)
N47	O3	1.201(3)	N47	O4	1.198(3)
C42	C51	1.471(4)	C43	C61	1.475(4)

Table 3. Selected Bond Angles(°) for I

atom	atom	atom	angle	atom	atom	atom	angle
C2	N1	C10	117.7(3)	C3	N4	C5	116.8(3)
O1	N7	O2	126.8(4)	O1	N7	C7	116.8(3)
O2	N7	C7	116.5(3)	C42	N41	C50 1	18.0(3)
C43	N44	C45	117.4(3)	O3	N47	O4	126.0(3)
O3	N47	C47	117.1(3)	O4	N47	C47	116.9(3)

Table 4. Selected hydrogen-bonding geometry(Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C31—H31···O1^{i}	0.93	2.46	3.391(6)	176
C71—H71···O3^{ii}	0.93	2.45	3.368(7)	169
C31—H31···O1A^{i}	0.93	2.32	3.22(2)	165
C71—H71···O3A^{ii}	0.93	2.21	3.11(3)	164

Symmetry codes: (i) 1 -x, 1 - y, 2 - z; (ii) - x, 2 - y, 1 - z.

APPENDIX IX*

Crystallographic data for 1,1'-bis(3-phenyl-2-quinoxalyl)-ferrocene (61)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{38}H_{26}Fe\ N_4$, 0.90($C\ H_2\ Cl_2$)
Formula Weight	594.28 + 76.5 = 670.78
Crystal Colour, Habit	purple, plates
Crystal Dimensions	0.42 X 0.28 X 0.01 mm
Crystal System	triclinic
No. of Reflections Used for Unit Cell Determination (2θ range)	25 (9.65 - 18.03)°
Omega Scan Peak Width at Half-height	
Lattice Parameters	a = 8.3216(16) Å b = 12.392(3) Å c = 15.949(2) Å α = 83.58(2)° β = 79.634(16)° γ = 72.990(15)° V = 1544.1(6) Å^3
Space Group	$P\bar{1}$
Z value	2
D_m	Not measured
D_x	1.443 Mg m^{-3}
F(000)	691
$\mu(M_o\ K_\alpha)$	0.680 mm^{-1}

* Following the university restriction for the size of thesis only selected data are presented here, for the detailed account of atomic coordinates, geometric parameters and anisotropic factors pleases refer to **Cambridge Crystallographic Database** ref. *Acta Crystallogr.* C, 1998, **54**, .

B. Intensity Measurements

Diffractometer	Enraf-Nonius CAD-4
Radiation	$M_o K_\alpha$ (λ = 0.7107 Å) graphite monochromated
Temperature	294 (1) K
Scan Type	$\theta/2\theta$
θ_{max}	25.45°
	h = -9 to 10
	k = 0 to 15
	l = -18 to 19
No. of Reflections Measured	Total: 5739
	2727 with > 2σ(I)
Absorption Correction	Gaussian ABSO in NRCVAX
3 standard reflections	frequency: 120 min
	intensity decay: 1.9%

C. Structure Solution and Refinement

Structure Solution	Patterson heavy-atom method and NRCVAX96 and SHELXL97
Extinction correction	none
Refinement on F^2	$R[F^2 > 2\sigma(F^2)] = 0.0674$
	$\omega R(F^2) = 0.1443$
	S = 0.852
Number of Reflections	5739
Number of parameters	416
H atom parameters	constrained
$w = 1/[\sigma^2(F_o^2) + (0.0617\ P)^2]$ where $P = (F_o^2 + 2Fc^2)/3$	
Max Shift/Error in Final Cycle $(\Delta/\sigma)_{max}$	0.012
Maximum peak in Final Diff. Map (ΔP_{max})	0.376 $e^-/Å^3$
Minimum peak in Final Diff. Map (ΔP_{min})	-0.273 $e^-/Å^3$

Table 1. Fractional Atomic coordinates and equivalent isotropic displacement parameters (Å^2)

atom	Occupancy	x	y	z	U_{eq}
Fe1	1	0.07300(10)	0.09663(6)	0.13964(5)	0.0382(2)
C11	1	0.2946(6)	0.1264(4)	0.1569(3)	0.0384(12).
C12	1	0.1598(6)	0.2286(4)	0.1576(3)	0.0441(13)
C13	1	0.0997(7)	0.2465(5)	0.0792(3)	0.0530(15)
C14	1	0.1950(7)	0.1558(5)	0.0278(3)	0.0529(15)
C15	1	0.3117(7)	0.0825(4)	0.0754(3)	0.0440(13)
C21	1	0.0317(6)	-0.0394(4)	0.2188(3)	0.0398(13)
C22	1	-0.0826(6)	0.0653(4)	0.2476(3)	0.0460(13)
C23	1	-0.1800(7)	0.1184(5)	0.1832(4)	0.0541(15)
C24	1	-0.1301(6)	0.0501(4)	0.1138(3)	0.0477(14)
C25	1	0.0009(6)	-0.0456(4)	0.1341(3)	0.0438(13)
N1	1	0.5049(5)	-0.0318(3)	0.2027(2)	0.0384(10)
C2	1	0.3961(6)	0.0675(4)	0.2236(3)	0.0332(11)
C3	1	0.3818(6)	0.1093(4)	0.3051(3)	0.0383(12)
N4	1	0.4683(5)	0.0494(3)	0.3645(3)	0.0428(11)
C5	1	0.5790(6)	-0.0540(4)	0.3438(3)	0.0392(12)
C6	1	0.6716(7)	-0.1193(4)	0.4056(4)	0.0545(15)
C7	1	0.7838(7)	-0.2205(5)	0.3850(4)	0.0623(16)
C8	1	0.8061(7)	-0.2603(5)	0.3039(4)	0.0569(16)
C9	1	0.7168(7)	-0.1979(4)	0.2427(4)	0.0529(15)
C10	1	0.5999(6)	-0.0924(4)	0.2622(3)	0.0383(12)
C31	1	0.2745(6)	0.2233(4)	0.3309(3)	0.0409(13)
C32	1	0.1270(7)	0.2324(5)	0.3866(3)	0.0526(15)
C33	1	0.0300(8)	0.3361(6)	0.4147(4)	0.0702(19)
C34	1	0.0832(10)	0.4305(6)	0.3868(5)	0.079(2)
C35	1	0.2324(10)	0.4226(5)	0.3321(5)	0.073(2)
C36	1	0.3293(7)	0.3174(5)	0.3029(4)	0.0573(16)
N41	1	0.1392(5)	-0.0857(3)	0.3490(3)	0.0421(11)
C42	1	0.1454(6)	-0.1185(4)	0.2722(3)	0.0361(12)
C43	1	0.2544(6)	-0.2266(4)	0.2452(3)	0.0377(12)
N44	1	0.3384(5)	-0.3000(3)	0.2990(3)	0.0465(11)
C45	1	0.3316(7)	-0.2678(4)	0.3796(3)	0.0459(13)
C46	1	0.4267(7)	-0.3426(5)	0.4376(4)	0.0586(16)
C47	1	0.4282(8)	-0.3108(5)	0.5159(3)	0.0629(17)
C48	1	0.3313(8)	-0.2013(5)	0.5386(3)	0.0585(16)
C49	1	0.2376(7)	-0.1266(5)	0.4852(3)	0.0534(15)
C50	1	0.2342(7)	-0.1604(4)	0.4034(3)	0.0436(13)
C51	1	0.2819(6)	-0.2656(4)	0.1582(3)	0.0390(12)
C52	1	0.3921(7)	-0.2288(4)	0.0944(3)	0.0469(14)
C53	1	0.4327(7)	-0.2731(5)	0.0147(4)	0.0558(15)
C54	1	0.3618(8)	-0.3522(5)	-0.0020(4)	0.0629(17)
C55	1	0.2528(8)	-0.3908(5)	0.0608(4)	0.0637(17)
C56	1	0.2141(7)	-0.3487(4)	0.1408(4)	0.0541(15)
C61	0.898(4)	0.6706(10)	-0.4739(6)	0.1920(5)	0.090(3)
Cl61	0.898(4)	0.8337(3)	-0.44894(18)	0.11461(15)	0.1035(10)
Cl62	0.898(4)	0.7299(3) -	0.5812(2)	0.26143(18)	0.1282(12)

$$U_{eq} = (1/3)\ \Sigma_i\ \Sigma_j\ U_{ij}\ a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$$

Table 2. Selected Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
N1	C2	1.333(5)	N1	C10	1.362(6)
C2	C3	1.425(6)	C3	N4	1.320(6)
N4	C5	1.376(6)	C5	C6	1.397(7)
C5	C10	1.399(6)	C6	C7	1.359(7)
C7	C8	1.398(7)	C9	C10	1.411(7)
N41	C42	1.321(6)	N41	C50	1.369(6)
C42	C43	1.443(6)	C43	N44	1.312(6)
N44	C45	1.375(6)	C45	C50	1.395(7)
C45	C46	1.409(7)	C46	C47	1.354(7)
C47	C48	1.409(8)	C48	C49	.352(7)
C49	C50	1.421(7)			

Table 3. Selected Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C2	N1	C10	117.7(4)	C3	N4	C5	117.4(4)
C42	N41	C50	117.5(4)	C43	N44	C45	118.4(4)

Table 4. Selected Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C12	C11	C2	N1 1	75.2(5)	C15	C11	C2	N1	-0.9(7)
C12	C11	C2	C3	-3.9(8)	C15	C11	C2	C3	180.0(5)
N4	C3	C31	C32	-75.3(6)	C2	C3	C31	C32	106.4(6)
N4	C3	C31	C36	100.7(6)	C2	C3	C31	C36	-77.7(6)
C22	C21	C42	C43	176.7(5)	C25	C21	C42	C43	-0.6(8)
N41	C42	C43	N44	6.5(7)	C21	C42	C43	N44	-171.7(5)
N44	C43	C51	C52	-100.8(6)	C42	C43	C51	C52	79.6(7)
N44	C43	C51	C56	71.8(6)	C42	C43	C51	C56	-107.8(6)

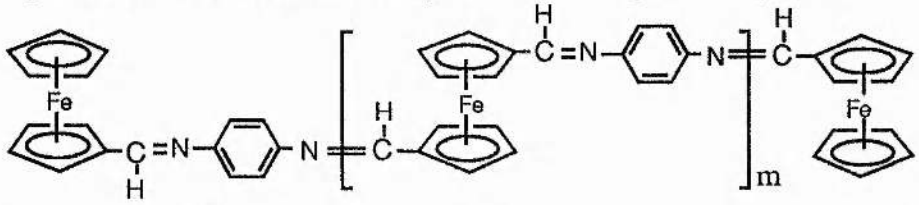
Table 5. Selected hydrogen-bonding geometry(Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C61—H61···N44	0.97	2.48	3.292(9)	141

APPENDIX X

Estimation of average molecular weight of ferrocene-containing polyimine (FCPI) polymer (73).

If the mono substituted ferrocenes are the end-groups in the ferrocene-containing polyimine (FCPI) **73**, the average molecular weight of the polymer can be estimated by taking the relative ratio of substituted and unsubstituted CP rings of ferrocene in the product. The integration of the representative peaks in the ^1H NMR spectrum was used as a tool to measure the relative amount of substituted and unsubstituted CP rings and simple calculations were performed to estimate the average molecular weight of the polymer.



Mol. wt. of the fragments. 302 314 198

Integration for the unsubstituted Cp ring peak = 7.7

Integration per proton = 7.7/10 = 0.77

Integration for the substituted Cp ring peak = 35.22

Av. No. of protons represented by substituted Cp ring peak = 35.22/0.77 = 45.74 ≈ 46

Av. No. of substituted Cp rings = 46/4 = 11.6 ≈ 12

Av. No. of substituted Cp rings in the repeating unit (m) = 12-2 = 10

m = 10/2 = 5

Av. molecular weight = 302 + 5x314 + 198 = 2070 ≈ 2.1 x 10^3

APPENDIX XI*

Crystallographic data for 4-ferrocenylketone-4'-biphenylcarbonylchloride (76)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{24}H_{17}ClFeO_2$
Formula Weight	428.68
Crystal Colour, Habit	red, plates
Crystal Dimensions	not measured
Crystal System	monoclinic
No. of Reflections Used for Unit Cell Determination (2θ range)	25 ()°
Omega Scan Peak Width at Half-height	
Lattice Parameters	a = 14.8547(9) Å b = 18.3258(17) Å c = 28.757(2) Å α = 90° β = 97.043(6)° γ = 90° V = 7769.3(10)Å^3
Space Group	Cc (No. 9)
Z value	4
D_m	Not measured
D_x	1.464 Mg m^{-3}
F(000)	880
$\mu(M_o K_\alpha)$	0.930 mm^{-1}

*Following the university restriction for the size of thesis only selected data are presented here.

B. Intensity Measurements

Diffractometer	Enraf-Nonius CAD-4
Radiation	$M_o K_\alpha$ (λ = 0.70930 Å) graphite monochromated
Temperature	293 (2) K
Scan Type	$\theta/2\theta$
θ_{max}	25.12°
	h = -8 to 8
	k = 0 to 10
	l = 0 to 27
No. of Reflections Measured	Total: 2838
	with > 2σ(I) 1858
Absorption Correction	Gaussian ABSO in NRCVAX

C. Structure Solution and Refinement

Structure Solution	Patterson heavy-atom method and NRCVAX96 and SHELXL97
Extinction correction	none
Refinement on F^2	$R[F^2 > 2\sigma(F^2)]$ = 0.0674
	$\omega R(F^2)$ = 0.1443
	S = 0.852
Number of Reflections	2838
Number of parameters	352
H atom parameters	constrained

Table 1. Fractional Atomic coordinates (Å^2)

Molecule = 1

atom	x	y	z
Fe(1)	0.39476(17)	0.07787(14)	0.28922(8)
Cl(1B)	0.2876(11)	0.4601(9)	0.6494(5)
O(11)	0.4625(6)	0.0091(5)	0.4053(3)
O(12B)	0.1187(11)	0.4314(18)	0.6128(13)
C(11)	0.3482(7)	0.0268(6)	0.3441(3)
C(12)	0.3738(7)	-0.0263(5)	0.3122(4)
C(13)	0.3227(8)	-0.0134(6)	0.2679(3)
C(14)	0.2656(7)	0.0477(6)	0.2724(3)
C(15)	0.2814(7)	0.0725(5)	0.3195(4)
C(16)	0.4995(7)	0.1408(7)	0.3130(3)
C(17)	0.5274(7)	0.0895(6)	0.2806(4)
C(18)	0.4731(7)	0.1001(6)	0.2370(3)
C(19)	0.4116(7)	0.1579(7)	0.2424(4)
C(110)	0.4279(7)	0.1831(6)	0.2894(4)
C(111)	0.3624(7)	0.1016(4)	0.4221(2)
C(112)	0.4263(5)	0.1457(5)	0.4478(3)
C(113)	0.3991(5)	0.1965(4)	0.4791(3)
C(114)	0.3079(6)	0.2031(4)	0.4848(2)
C(115)	0.2439(4)	0.1590(4)	0.4591(3)
C(116)	0.2711(6)	0.1082(4)	0.4277(3)
C(117)	0.3931(8)	0.0428(6)	0.3914(3)
C(121)	0.2260(5)	0.3630(4)	0.5801(2)
C(122)	0.3126(5)	0.3331(4)	0.5866(2)
C(123)	0.3374(5)	0.2807(4)	0.5556(3)
C(124)	0.2757(6)	0.2584(3)	0.5180(3)
C(125)	0.1891(5)	0.2883(4)	0.5115(2)
C(126)	0.1642(4)	0.3406(4)	0.5425(3)
C(127)	0.1988(7)	0.4188(4)	0.6132(3)
Disordered Atoms with S.O.F < 0.5			
Cl(1A)	0.0844(7)	0.4411(8)	0.6126(6)
O(12A)	0.256(2)	0.4486(18)	0.6406(10)
Molecule = 2			
Fe(2)	0.39785(16)	0.58005(14)	0.29418(8)
Cl(2)	0.3083(4)	1.0914(3)	0.5909(2)
O(21)	0.5590(6)	0.5868(5)	0.3964(3)
O(22)	0.2918(7)	0.9830(6)	0.6477(3)
C(21)	0.4970(7)	0.6415(6)	0.3265(3)
C(22)	0.5317(6)	0.5957(6)	0.2931(4)
C(23)	0.4838(7)	0.6113(6)	0.2484(3)
C(24)	0.4194(7)	0.6669(6)	0.2541(3)
C(25)	0.4276(7)	0.6855(5)	0.3024(3)
C(26)	0.3436(9)	0.5220(7)	0.3418(3)
C(27)	0.3765(8)	0.4751(6)	0.3084(4)
C(28)	0.3299(9)	0.4923(7)	0.2637(3)
C(29)	0.2681(8)	0.5498(7)	0.2694(4)

C(210)	0.2766(8)	0.5682(6)	0.3177(5)
C(211)	0.4794(6)	0.6946(4)	0.4096(3)
C(212)	0.4470(6)	0.6714(3)	0.4505(3)
C(213)	0.4211(6)	0.7223(5)	0.4821(2)
C(214)	0.4275(5)	0.7964(4)	0.4729(3)
C(215)	0.4598(6)	0.8196(3)	0.4320(3)
C(216)	0.4858(6)	0.7687(5)	0.4004(2)
C(217)	0.5160(8)	0.6404(6)	0.3778(3)
C(221)	0.3415(5)	0.9483(4)	0.5717(2)
C(222)	0.3638(6)	0.8768(4)	0.5845(2)
C(223)	0.3915(6)	0.8286(3)	0.5518(3)
C(224)	0.3970(5)	0.8520(4)	0.5062(3)
C(225)	0.3747(6)	0.9235(4)	0.4934(2)
C(226)	0.3469(6)	0.9716(3)	0.5262(2)
C(227)	0.3129(4)	0.9992(4)	0.6074(3)

Molecule = 3

Fe(3)	0.11857(16)	0.33022(14)	0.20654(9)
Cl(3A)	0.2316(5)	0.7136(5)	-0.1530(3)
O(31)	0.0486(7)	0.2609(5)	0.0906(3)
O(32A)	0.3925(9)	0.6944(10)	-0.1207(6)
C(31)	0.1680(6)	0.2855(6)	0.1507(3)
C(32)	0.1344(6)	0.2306(5)	0.1788(3)
C(33)	0.1838(7)	0.2348(5)	0.2243(3)
C(34)	0.2479(6)	0.2922(6)	0.2242(3)
C(35)	0.2381(6)	0.3236(5)	0.1787(4)
C(36)	0.0200(8)	0.4058(6)	0.1821(3)
C(37)	-0.0173(7)	0.3479(6)	0.2063(4)
C(38)	0.0273(8)	0.3467(6)	0.2529(4)
C(39)	0.0922(8)	0.4039(7)	0.2575(3)
C(310)	0.0877(8)	0.4405(6)	0.2137(4)
C(311)	0.1502(6)	0.3556(4)	0.0743(2)
C(312)	0.0874(4)	0.3984(5)	0.0468(3)
C(313)	0.1168(5)	0.4491(4)	0.0160(3)
C(314)	0.2089(6)	0.4569(4)	0.0127(2)
C(315)	0.2716(4)	0.4140(4)	0.0403(3)
C(316)	0.2423(5)	0.3634(4)	0.0711(3)
C(317)	0.1170(7)	0.2986(6)	0.1047(3)
C(321)	0.2884(5)	0.6165(4)	-0.0836(2)
C(322)	0.2021(5)	0.5863(4)	-0.0914(2)
C(323)	0.1760(5)	0.5334(4)	-0.0610(3)
C(324)	0.2363(6)	0.5109(4)	-0.0230(3)
C(325)	0.3226(5)	0.5411(4)	-0.0152(3)
C(326)	0.3487(4)	0.5940(4)	-0.0456(3)
C(327)	0.3178(6)	0.6726(4)	-0.1160(2)

Disordered Atoms with S.O.F < 0.5

Cl(3B)	0.4349(8)	0.6848(11)	-0.1144(7)
O(32B)	0.274(3)	0.7120(13)	-0.1438(8)

Molecule = 4

Fe(4)	0.11508(18)	0.82839(13)	0.20849(9)
Cl(4A)	0.1950(5)	1.3447(3)	-0.0889(3)
O(41)	-0.0497(5)	0.8318(5)	0.1060(3)
O(42A)	0.2312(11)	1.2365(19)	-0.1364(5)
C(41)	0.0158(7)	0.8932(6)	0.1745(3)
C(42)	-0.0214(7)	0.8413(5)	0.2034(4)
C(43)	0.0182(7)	0.8530(6)	0.2503(3)
C(44)	0.0799(7)	0.9122(6)	0.2503(3)
C(45)	0.0784(7)	0.9371(5)	0.2035(4)
C(46)	0.1806(8)	0.7760(7)	0.1588(3)
C(47)	0.1349(7)	0.7246(6)	0.1845(4)
C(48)	0.1701(7)	0.7310(6)	0.2325(4)
C(49)	0.2374(7)	0.7863(6)	0.2365(3)
C(410)	0.2440(6)	0.8142(6)	0.1910(4)
C(411)	0.0298(6)	0.9407(4)	0.0925(3)
C(412)	0.0626(6)	0.9160(3)	0.0521(3)
C(413)	0.0893(6)	0.9658(5)	0.0200(3)
C(414)	0.0832(6)	1.0402(5)	0.0283(3)
C(415)	0.0504(6)	1.0649(3)	0.0687(3)
C(416)	0.0237(6)	1.0151(5)	0.1008(3)
C(417)	-0.0033(7)	0.8839(6)	0.1236(3)
C(421)	0.1661(6)	1.1973(4)	-0.0690(2)
C(422)	0.1478(7)	1.1262(4)	-0.0842(2)
C(423)	0.1212(7)	1.0744(3)	-0.0533(3)
C(424)	0.1129(6)	1.0937(4)	-0.0073(3)
C(425)	0.1312(6)	1.1647(5)	0.0079(2)
C(426)	0.1578(6)	1.2166(4)	-0.0230(3)
C(427)	0.1992(5)	1.2520(5)	-0.1006(3)

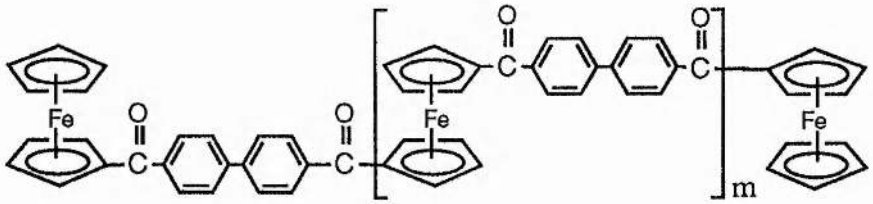
Disordered Atoms with S.O.F < 0.5

Cl(4B)	0.2101(11)	1.2196(11)	-0.1556(4)
O(42B)	0.2182(13)	1.3148(8)	-0.0911(9)

APPENDIX XII

Estimation of average molecular weight of ferrocene-containing polyketone (FCPK) polymer (85).

If the mono substituted ferrocenes are the end-groups in the ferrocene-containing polyketone (FCPK) **85**, the average molecular weight of the polymer can be estimated by taking the relative ratio of substituted and unsubstituted CP rings of ferrocene in the product. The integration of the representative peaks in the ^1H NMR spectrum was used as a tool to measure the relative amount of substituted and unsubstituted CP rings and simple calculations were performed to estimate the average molecular weight of the polymer.



Molecular weights of the fragments 393 392 185

Integration for the unsubstituted Cp ring peak = 9.86

Integration per proton = 9.86/10 = 0.986

Integration for the substituted Cp ring peak = 29.12

Av. No. of protons represented by substituted Cp ring peak = 29.12/0.986 = 29.54 ≈ 30

Av. No. of substituted Cp rings = 30/4 = 7.5 ≈ 8

Av. No. of substituted Cp rings in the repeating unit (m) = 8-2 = 6

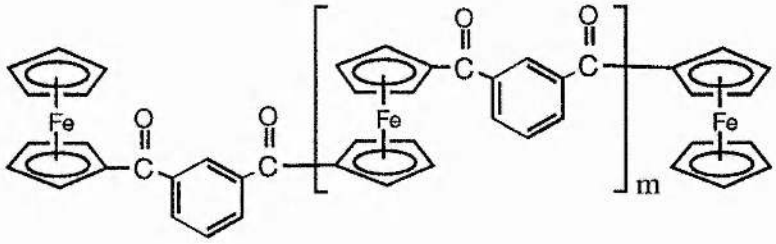
Av. No. of repeating units, m = 6/2 = 3

Av. molecular weight = 393+ 3x392+ 185 = 1754 ≈ 1.75 x 10^3

APPENDIX XIII

Estimation of average molecular weight of ferrocene-containing polyketone (FCPK) polymer (87).

If the mono substituted ferrocenes are the end-groups in the ferrocene-containing polyketone (FCPK) **87**, the average molecular weight of the polymer can be estimated by taking the relative ratio of substituted and unsubstituted CP rings of ferrocene in the product. The integration of the representative peaks in the ^1H NMR spectrum was used as a tool to measure the relative amount of substituted and unsubstituted CP rings and simple calculations were performed to estimate the average molecular weight of the polymer.



Molecular weights of the fragments 317 316 185

Integration for the unsubstituted Cp ring peak = 19.29

Integration per proton = 19.29/10 = 1.93

Integration for the substituted Cp ring peak = 403.93

Av. No. of protons represented by substituted Cp ring peak = 403.93/1.93 = 209.3 ≈ 209

Av. No. of substituted Cp rings = 209/4 = 52.25 ≈ 52

Av. No. of substituted Cp rings in the repeating unit (m) = 52-2 = 50

Av. No. of repeating units, m = 50/2 = 25

Av. molecular weight = 393+ 25x392+ 185 = 10378 ≈ 1.04×10^4

APPENDIX XIV

List of lecture courses completed during Ph.D. studies.

Following are the ***Lecture Courses*** attended and completed successfully during the period of 1995-1998, as the partial requirement for the degree of Ph.D. by the School of Chemistry, University of St. Andrews.

No.	Course Title	Lecturer
1.	Introduction to Instrumental Methods	Dr. R.K. Mackie
2.	Presentational Skills	Dr. C. Mason
3.	Transition Metals in Organic Chemistry	Dr. C. Glidewell
4.	Advanced NMR	Dr. R.K. Mackie
5.	High Resolution NMR	Dr. J. Richardson and Dr. C. Weller
6.	Introduction to X-ray Crystallography	Dr. P. Lightfoot
7.	Advanced Inorganic Electrochemistry	Dr. J.A. Cryston
8.	Redox Reactions of Environmental Significance	Dr. I. Fábián
9.	Safety in the Chemistry Laboratory	Dr. R.A. Aitken

APPENDIX XV

List of publications.

Following are the publications (so far) from the results of the research in this thesis, carried out during the period 1995-1998 at School of Chemistry, University of St. Andrews, Scotland.

1. Racemic (α-Ferrocenylphenacyl)triphenylphosphonium Iodide

   S. Zaka Ahmed, Christopher Glidewell and George Ferguson.
   Acta Crystallogra., 1996, **C52**, 1634-1634.

2. Synthesis of ferrocenyl-1,2-diketones and related compounds: crystal and molecular structures of 1,2-diferrocenylethanedione and 1-ferrocenyl-2-(4- biphenylyl)ethanedione.

   Christopher Glidewell, S. Zaka Ahmed, Michael Gottfried, Philip Lightfoot, Brodyck J.L. Royles, Jeremy P. Scott and Jörg Wonnemann.
   J. Organomet. Chem., 1997, **530**, 177-185.

3. Oxidation of ferrocenyl ketones using selenium(IV) oxide: Crystal and molecular structures of racemic 2,3-diferrocenyl-1,4-diphenylbutane-1,4-dione, racemic and meso 2,3-diferrocenyl-1,4-bis(4-biphenylyl)butane-1,4- dione and ferrocenylmethyl(4-biphenylyl)-ketone.

   S. Zaka Ahmed, Christopher Glidewell and Philip Lightfoot.
   J. Organomet. Chem., 1997, **542**, 81-88.

4. Synthesis and redox properties of ferrocenylquinoxalines.

   Piero Zanello, Marco Fontani, S. Zaka Ahmed and Christopher Glidewell.
   Polyhedron, 1998, in press.

5. 3-Ferrocenyl-2-phenyl-6-nitroquinoxaline: cyclic centrosymmetric dimers depending on both C—H···O hydrogen bonds and π-π stacking interactions.

   S. Zaka Ahmed, George Ferguson and Christopher Glidewell. *Acta Crystallogra.*, 1998, **C54**, in press.

6. 1,1'-Bis(3-phenylquinoxaline-2-yl)ferrocene.

   S. Zaka Ahmed, Christopher Glidewell and George Ferguson. *Acta Crystallogra.*, 1998, **C54**, in press.

The following two publications are the result of the work carried out as a side interest developed while carrying out the main thesis research during the above period, but is not included in the thesis.

7. Accurate Redeterminations of 1,1'-Dibenzoylferrocene and (4-Nitrophenyl)-ferrocene.

   John F. Gallagher, George Ferguson, S. Zaka Ahmed, Christopher Glidewell and Arwel Lewis.
   Acta Crystallogra., 1997, **C53**, 1772-1775.

8. 1'-Benzoylferrocenyl)diphenylmethanol; a Centrosymmetric $R^4_4(16)$ Dimer Generated by C—H···O Hydrogen Bonding.

   Christopher Glidewell, S. Zaka Ahmed, John F. Gallagher and George Ferguson.
   Acta Crystallogra., 1997, **C53**, 1775-1778.